International Journal of Air Pollution

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1959/60

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PERGAMON PRESS London New York Paris Los Angeles

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Int. J. Air Poll. Pergamon Press 1959. Vol. 2, pp. 1–26. Printed in Great Britain

ATMOSPHERIC DEPOSITS IN BRITAIN A STUDY OF DINGINESS

W. F. CAREY
Consultant to Head Wrightson Ltd., Thornaby-on-Tees
(*Received* 13 *February* 1959)

Abstract—Since it has been estimated that equipment to provide cleanliness might cost Great Britain over £500,000,000, discussions about the economics of treatment seem likely to delay progress in satisfying the public demand until some yardstick of cleanliness becomes accepted widely. Dinginess is a major aspect of the dust nuisance and is caused by a light deposit of atmospheric dust which remains invisible as it accumulates until it covers more than about 0·4 per cent of the surface of the ground (Fig. 3). At intervals of about 10 days the deposit is washed off the surface by heavy showers so that rate of coverage is a rational measure of nuisance. In the same way cleanliness is proportional to the average number of clean days in ten, which is a convenient yardstick for describing the amenity of a district. When dust is discharged from chimneys it mixes with the wind, the coarse fractions settle within a mile and the fines less than 30 μ spread across the country leaving a trace on the ground which becomes objectionable in cities rather than in rural areas because:

(a) Being populated densely, cities emit up to a hundred times as much dust as an equal area in the country so that there is a corresponding increase in the concentration at ground level.
(b) Dust deposited on vegetation is less conspicuous than dust deposited on built-up areas.

There is broad agreement between practical observations of dinginess and a theoretical approach based on the optics of deposited particles. However, in view of the empirical nature of the earlier systems of measuring dinginess the virtue of this comparison rests principally on the wide range of coverages which have been observed.

Present practice in controlling dust emissions aims at a rate of deposit in the neighbourhood which will not exceed that deemed tolerable by previous experience. As the weight deposited per unit area includes no allowances for the important influence on nuisance exerted by the fineness of the particles and by the nature of the ground, there has been some confusion: an important result has been to underestimate the effect of fine particles. Until the results of further work are available it would appear to be advisable to measure the dinginess-nuisance of deposits in terms of their coverage as is described in this paper. Emissions would then be controlled on a more rational basis and there would be no serious conflict with such data as are available.

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1. INTRODUCTION

A LIGHT deposit of dust causes surfaces to assume a dingy appearance. This is a notorious feature of atmospheric pollution in Britain where there are hundreds of installations for treating chimney gases so as to control the deposits in their neighbourhood. The rate of deposit depends upon the product of the falling speed of the suspended particles and of their concentration near the ground; it is controlled by treating chimney effluents to remove the large particles and by adjusting the height of emission so that the exit concentration will be diluted by the wind before it spreads to the ground level. Judicious application of such measures implies some knowledge of the connexion between nuisance and deposit. The following study can be regarded as an approach to this important and controversial question.

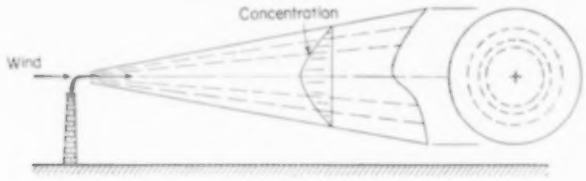
2. FORMATION OF DUST DEPOSITS

2.1. *Spread of dust*

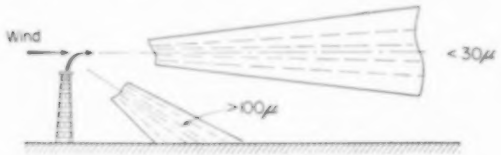
When a stream of cold smoke is discharged into the wind it establishes a horizontal

plume comprising an axial zone of high concentration which diminishes outwards radially. As it travels downwind the eddies act on the concentration gradient to spread the plume. Although the concentrations become diluted atmospheric turbulence preserves this pattern of dust distribution almost indefinitely. This behaviour applies to hot emissions of smoke as well as to cold if an allowance is made for the initial thermal rise, i.e. the hot plume is imagined to spread horizontally from a false source elevated above the top of the chimney.

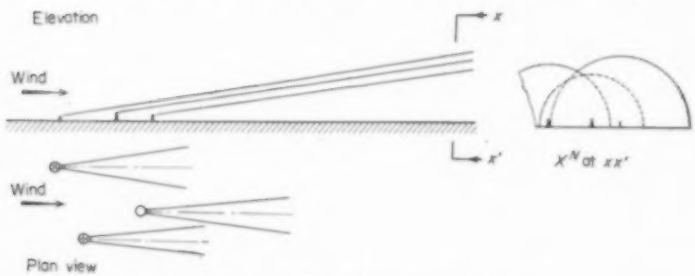
Dust particles spread in the same manner as smoke but the axes of their plumes incline downwards according to their fall in the wind. Fig. 1 (b) shows how in normal winds particles greater than 100 μ will deposit on the ground near the stack whilst particles less than 30 μ continue to spread continuously so that the plume will attain a height of several thousand feet after travelling 10–20 miles. Much of this fine dust blows right across the country and out to sea.



(a) Formation of smoke plume.



(b) Plumes of fine and coarse dust from single source.



(c) Combination of plumes from multiple sources.

FIG. 1. Behaviour of wind-blown dust.

The sources of fine dust in Britain are so numerous that the country can be divided into industrial areas in which the strength of emission is great and country areas in which the strength is slight. The plumes from these areas mingle so that the ground concentrations everywhere are influenced by every change in the wind, consequently the rates of deposit are highly variable both in time and space. Nevertheless the

scale of the spreading is considerable so that rates of deposit measured at points 100 yd apart do not differ provided that they are remote from large dust sources.

2.2. *Measurement of deposit*

The rate of dust deposit can be measured by observing the discoloration of a horizontal sheet of clean white paper; a simple experiment of this nature can be carried out in a dusty room. The observations can be made by placing a rubber bung in the middle of the paper (Fig. 2) and removing it for inspection from time to time until the circle beneath the bung appears cleaner than its surroundings. If the dust concentration is maintained throughout, e.g. by ventilating the room with dusty air, the particles will descend more or less continuously on to the paper, nevertheless it will remain apparently clean for a period and will then almost suddenly become dirty. The subsequent dingy appearance occurs when the surface is covered with specks of dust whose spacing is closer than some critical value, say 10 to 20 diameters apart. Further deposits reduce the separation between the particles and slowly darken the deposit. The duration of the clean period varies from a few hours to many days and can be used to measure the rate at which surface dust is deposited from the atmosphere.

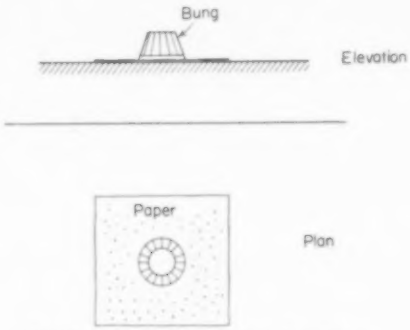


FIG. 2. Experiment on dust deposition.

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3. VISIBILITY OF DUST DEPOSITS

3.1 *Single particles*

A surface often appears dusty, although the individual particles are too small to be distinguished. When it is viewed at a distance of 10 in., a circle 100 μ (0·1 mm) in diameter subtends an angle of just over 1/60 of a degree of angular measure and can scarcely be perceived; it cannot be focused at less than 10 in. and will appear smaller at greater distances and in consequence is the smallest dot visible to the human eye. Furthermore, particles less than about 1 mm (1000 μ) will not be visible on the ground from the standing position. 1 mm particles fall at over 10 ft/sec and are about the largest particles likely to be discharged from chimneys; it seems therefore that dust deposits are revealed by differences in reflection since individual particles are too small to be perceived by the public.

3.2 *Layer of single particles*

Surfaces which receive deposits of fine particles appear dirty when the cover is sufficiently dense to reduce the reflection of light perceptibly. The least perceptible

cover concerns the sensitivity of the eye and can be evaluated by experiments with specially prepared patterns such as are shown in Fig. 3. If the charts in Fig. 3 are viewed at a distance too great to perceive individual dots it will be found that when the contrast is strong, e.g. black on white, it is possible to distinguish the clean circle from its surroundings when 0·2 per cent of the area is covered with dots; with a weaker colour contrast 0·4 per cent is the limiting coverage. The effect is subjective, nor is it easy to judge between coverages which differ by a factor of $\sqrt{2}$. Bearing in mind the difficulties of measurement it seems that values of 0·2 per cent for strong contrasts and 0·4 per cent for weak, apply to the majority of observers.

Deposited particles will rest on their two major dimensions and low critical coverages will be some 10 to 20 diameters apart. Thus unless viewed very obliquely the fraction of the surface covered will be independent of the angle of view.

4. IMPERCEPTIBLE RATES OF DEPOSIT

In Britain the atmosphere invariably contains dust which continually falls upon exposed surfaces ; in the absence of some cleansing agency all surfaces would become dirty and remain so permanently.

TABLE 1. PROGRESS OF DEPOSITS ON SURFACES EXPOSED TO A DUSTY ATMOSPHERE

(a) INDOORS AND UNDISTURBED

Date of examination (days from zero)	Condition of surface	% Surface covered by dust particles	Separation between adjacent particle diameters
0	Clean	—	50*
10	Neutral	0·4	16
20	Dirty	0·8	11
40	Dirty	1·6	8

* Guessed allowance for imperfect cleaning.

(b) OUTDOORS, EXPOSED TO INTERMITTENT HEAVY SHOWERS

Date of examination (days from zero)	Hypothetical incidence of rainstorms (days from zero)	Days exposure after rain when examined	Condition of surface
0	0	0	Clean
10	12	10	Neutral
20	17	3	Clean
30	28	—	—
40	—	12	Dirty

4.1 *Effect of rainstorms*

The cleanliness of apartments is maintained by periodic dusting (Table 1 (a)) whereby particles which settle from the atmosphere are swept up : outdoor dust settles in the same way, but the deposits are removed by heavy rain (say, 0·1 in/hr = 2540 μ/hr) which is thought to occur at average effective intervals of about 10 days (Table 1 (b)). The colour contrast between the particles and the ground is usually

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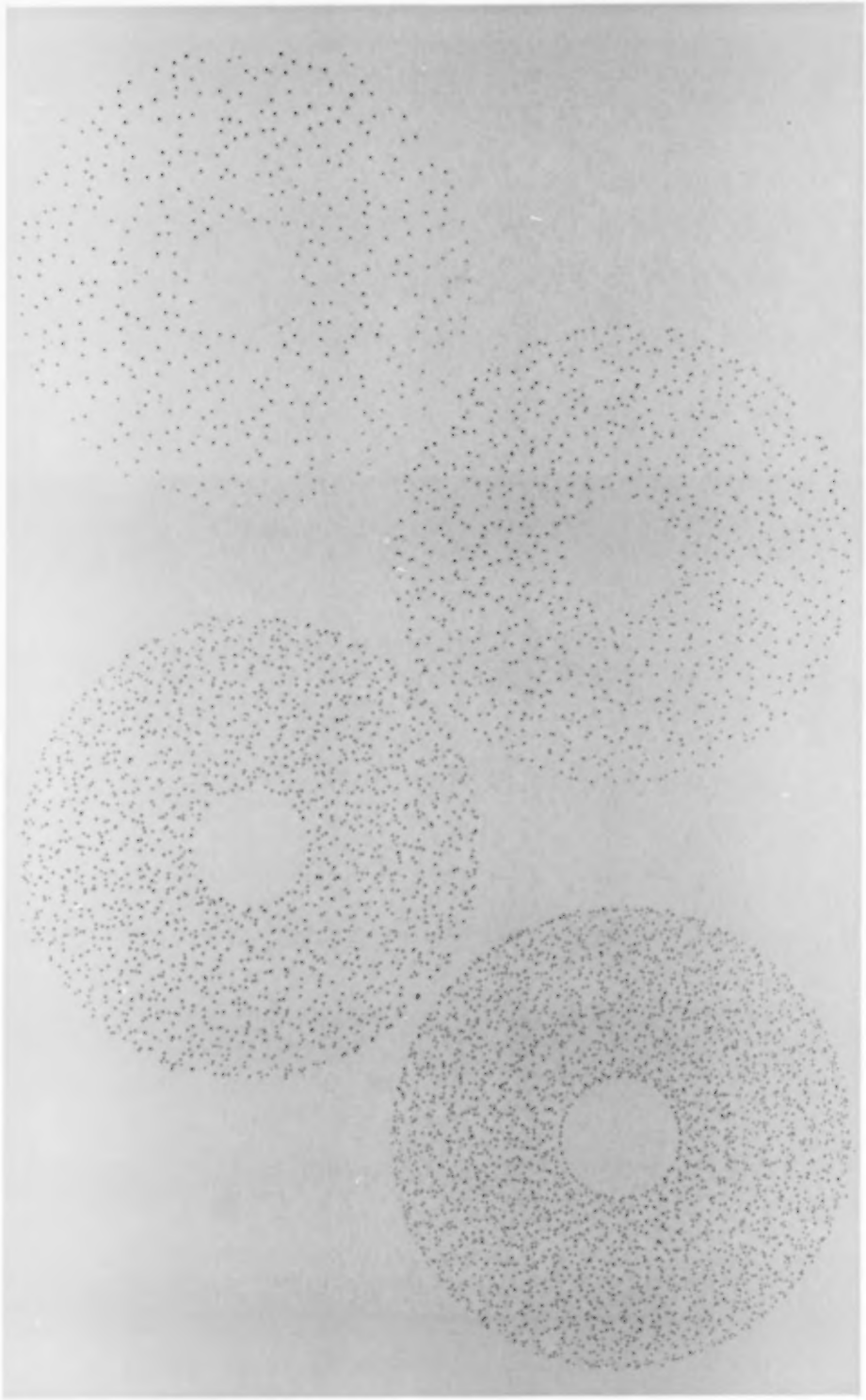
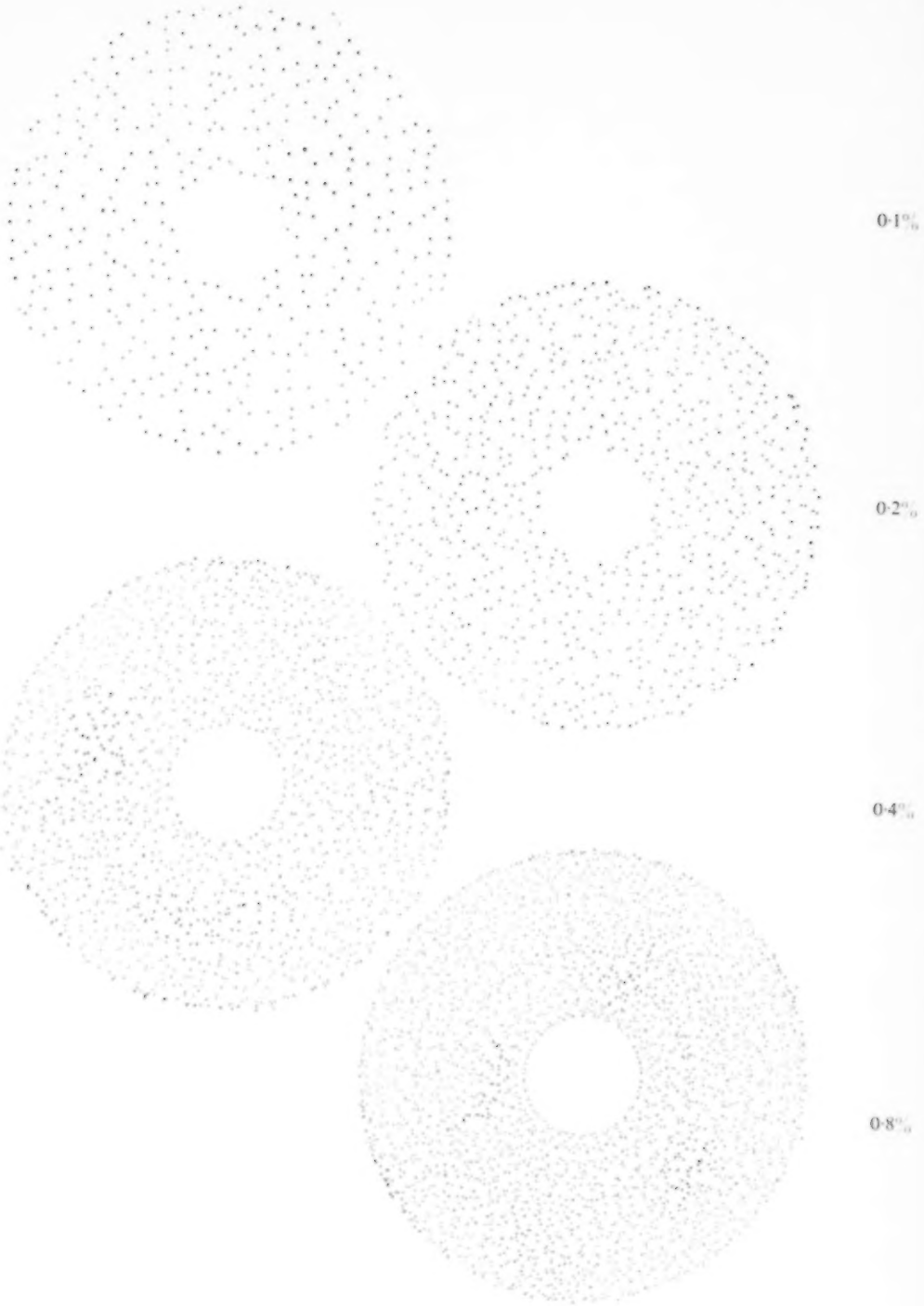


FIG. 3. Dust deposits and coverage—% surface covered.
with dots so that the areas covered are 0·1%, 0·2%, 0
contrast between the outer dotted area and the inner bl
individual dots, it is just possible to detect 0·2% cover
grey.)



ered. (Each annular ring is marked at random
%, 0·4% and 0·8% of the total. By noting the
er blank circle at a distance too great to perceive
coverage on the white and 0·4% coverage on the

not very pronounced, so that if the atmosphere does not deposit a coverage of 0·4 per cent in 10 days the deposit would seldom be visible; 0·04 per cent per day might be judged a tolerable rate of deposit because it would rarely be noticeable except in droughts, etc.

The situation described in Table 1 (a) is that of a room ventilated with an atmosphere which deposits dust at a steady rate of 0·04 %/day, so that the surfaces (if undisturbed) appear clean for 10 days then dirty. Table 1 (b) considers the impression which will result from the same atmosphere out of doors: if each change of wind affected the rate of coverage, 0·04%/day (or any other) would be a 10-day average which could be measured by timing the period of apparent cleanliness. It is seen that departures from the average interval between storms—10 days—exaggerate the degree of cleanliness or of dirtiness. These variations are not thought to be very important and their effects have been assumed to about cancel so that the public will deem tolerable a long-term rate of coverage whose deposits just become visible in 10 days, or whatever interval is found appropriate.

4.2 *Rural districts*

Coverages four or five times as great as the critical figure of 0·04%/day would probably escape notice when deposited on grassland and vegetation because:

(a) The area of the foliage is at least twice that of the surface of the ground which supports it.

(b) Much of the foliage is rarely stationary or horizontal so that some of the dust will fall directly on to the roots without adhering to it and some will soon be dislodged by the action of the wind.

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TABLE 2. MAXIMUM COVERAGE LIKELY TO BE IMPERCEPTIBLE IN VARIOUS SITUATIONS

Description of situation		Duration of period of undisturbed growth	Coverages on earth's surface		Remarks
			Smallest perceptible (%)	Max. rate for cleanliness (%/day)	
Floors, shelves and furniture indoors		Between dustings: Daily	0·2	0·2	Walls remain clean 10–100 times as long as floors according to the adhesion of dust
		Between dustings: Weekly		0·03	
Roads and pavements	Urban	Between heavy rainstorms at average intervals of ten days	0·4	0·02	Deposits from the atmosphere augmented by those from local sources
	Rural		0·4	0·04	
Grassland and vegetation			2	0·2	Areas greater than the ground are available to receive dust some of which becomes detached

4.3 *Urban areas*

There is little or no vegetation in cities and dust deposits accumulate in hollows, gutters, etc.; under the action of the wind these deposits can become subsidiary dust sources. This dust bowl action seems likely to increase the rate of deposit on dusty sites so that it will exceed the atmospheric rate by a factor here guessed at 2 and later found to agree roughly with other observations.

Very little of the dust which has fallen on vegetation will be re-entrained later by changes in the direction of the wind or by increases in its strength.

4.4 *Acceptable coverages*

There appears to be a *prima facie* case for avoiding dinginess by controlling the rate of atmospheric coverage on the principle that the public will not be inconvenienced by a nuisance which they are unable to perceive. The coverages given in Table 2 are the result of applying this principle to the situations discussed in Sections 4.2 and 4.3.

4.5 *Percentage cleanliness*

The inhabitants of a district will judge its degree of cleanliness in terms of the fraction of the time over which it appears clean. In this way, if the atmospheric

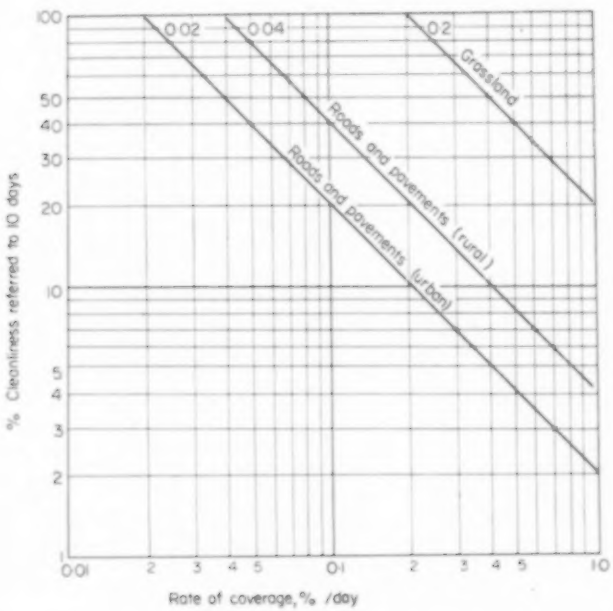

FIG. 4. Coverage and cleanliness (Logarithmic scales).

coverage was twice the critical, the district would appear clean for 5 days and dirty for 5; the corresponding cleanliness would then be 50 per cent and so on: if referred to a period of N days between storms

$$\% \text{ Cleanliness} = \frac{\text{Minimum noticeable coverage } \%}{N \times \% \text{ Daily coverage}} \times 100$$

$$= 10 \times \frac{\text{Minimum noticeable coverage } \%}{\% \text{ Daily coverage}}$$

for a period of 10 days between storms.

Since percentage cleanliness appears to be an adequate yardstick for relating cleanliness to experience Fig. 4 shows percentage cleanliness for various rates of coverage in several types of district.

4.6 *Standards of cleanliness*

Dingy districts in Britain experience rates of coverage greater than 1%/day, which is about a thousand times that in clean rural areas, so that dinginess could be controlled by specifying a maximum rate for each district. Coverages corresponding to 100% cleanliness could include an allowance for the topography. However, it would be better to set the standards at 50% cleanliness instead of 100% because:

(a) Coverages less than those corresponding to 100% cleanliness would appear no better than clean to the public but might cost more to maintain.

(b) Owing to the vagaries of the intervals between storms and of the weather the public would have difficulty in distinguishing between 50% and 100% cleanliness. Also departures from 50% cleanliness to 40% or 60% would be more easily recognizable than departures from 100% to either 80% or 120%.

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4.7 *Recapitulation*

The preceding sections have developed a rational system for standards of cleanliness by considering the balance between the rates of deposit and removal of dust. The argument has included approximations and assumptions which may be falsified in the light of later experience. It is collected in Table 3 in a form which permits the effect of such aberrations to be estimated readily.

5. ARITHMETIC OF DEPOSITION

This section develops arithmetical relationships between the concentration and the grading of the dust in the atmosphere near ground level and the resultant rates of deposit and coverage. In the situations where dust is suspended in a turbulent wind which blows horizontally over a streamline film in contact with flat surfaces gravity is the controlling agent of deposition.

There are other mechanisms:

(i) Particles $> 20\,\mu$ can be impinged e.g. when the wind blows across twigs or wires,

(ii) Particles $< 1\,\mu$ diffuse e.g. above hot water pipes.

The last two mechanisms cannot be ignored and there are others; however their influence on the national dust nuisance is thought to be minor in comparison with that of gravity.

5.1 *Deposit of uniform particles*

When a dilute dust cloud, whose volumetric concentration = V, falls under gravity at a speed f on to a horizontal surface the volume of solid deposited on unit area accumulates at a rate fV. In c.g.s. units the depth of the deposited layer increases

TABLE 3. LIST OF SYMBOLS

No.	Symbol	Significance	Units	Derivation	Assumed value	Relevant section
1	C_e	Critical coverage	%	% area covered by dust deposit which is barely visible	0·4% on plain surfaces	3·2
2	C_D	Daily rate of coverage	% per day			
3	F_B	Dust bowl factor	—	$\frac{\text{Vol. of dust re-entrained}}{\text{Vol. of dust deposited}} + 1$	2	4·3
4	F_G	Grassland factor	—	$\frac{\text{Critical coverage on grassland}}{\text{Critical coverage for plain surfaces}}$	5	4·2
5	P_e	% cleanliness	%	Number of apparently clean days in 100 days	—	4·5
6	$\frac{S}{10}$	Storm interval factor		For use if it should prove that the interval between storms differs from the guessed value of 10 days	10	4·1

Number of days to accumulate a perceptible covering $= \frac{C_e}{C_D}$ days.

Number of clean days in 10 $= \frac{C_e}{C_D}$.

% Cleanliness $= 10\frac{C_e}{C_D}$.

If the interval between storms is S days

% Cleanliness $= \frac{10}{S} \times \left(10 \times \frac{C_e}{C_D}\right)$.

If the deposit falls on grassland

% Cleanliness $= F_G \times \left(10 \times \frac{C_e}{C_D}\right) \cdot F_G = 5.$

If there is dust-bowl action

% Cleanliness $= \frac{1}{F_B} \times \left(10 \times \frac{C_e}{C_D}\right) \cdot F_B = 2.$

at fV cm/sec; these units may prove inconvenient sometimes and can be converted as follows:

A rate of growth of 1 cm/sec $= 0{\cdot}864 \times 10^9$ μ/day.

A concentration of 1 vol/vol $= 10^9\sigma$ mg/m^3 where σ is the specific gravity of the solid.

This leads to the formulae given in Table 4.

TABLE 4

Concentration of suspension (mg/m³)	Free falling speed of particles	Rate of growth of deposited layer (μ/day)	
		Sp. gr. $=\sigma$	Sp. gr. $=2$
M	f(cm/sec)	$(0{\cdot}864/\sigma)\,Mf$	$0{\cdot}432Mf$
M	F(ft/sec)	$(26{\cdot}4/\sigma)\,MF$	$13{\cdot}2MF$

The specific gravity of most solids is about 2 and they fall as shown in Table 5.

TABLE 5. FALLING SPEEDS OF SOLIDS (SP. GR. $=2$) IN ATMOSPHERIC AIR

Particulars		B.S.S. grade intervals (Extrapolated)						Stokes region formula
Diameter in microns		19	27	37	53	76	103	D
Free falling speed	cm/sec	2·3	4·6	9·2	15·3	29	46	$f=61\times(D/100)^2$
	ft/sec	0·075	0·15	0·30	0·50	0·95	1·5	$F=2\times(D/100)^2$

Practically all solids are much denser than the atmosphere so that their fall varies as σ, therefore the volume of the layer deposited is nearly independent of its specific gravity. This circumstance permits the values given in Table 5 to be used in estimating the rate of growth of solid layers of any specific gravity. Furthermore in grades less than 76 μ which fall more or less according to Stokes's law, the rate of growth of deposit in microns per day for ground concentrations of 1 mg/m³ is

$$26{\cdot}4\times[(\text{Diameter in microns})/100]^2.$$

5·2 *Deposit of mixed sizes*

The rate of deposit from a cloud of mixed sizes can be found by summating the rates from the individual grades of size; the formulae in Table 4 can be applied as shown in Table 6.

TABLE 6. CALCULATION OF DEPOSIT FROM A CONCENTRATION OF 0·1 mg/m³ AT GROUND LEVEL

Sample grading of cloud			Mean falling speed (ft/sec) (See Table 5)	Rate of deposit (μ/day) [$=1{\cdot}32\times$(Falling speed in ft/sec)]
Size range of grades	Mean size μ	% Within grade %		
106–76	91	5	1·20	0·079
76–53	65	15	0·77	0·153
53–37	45	35	0·40	0·185
37–27	32	30	0·20	0·087
27–19	23	10	0·11	0·014
<19	9·5	5	0·02	0·002
		100		0·530

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5.3 *Rate of coverage*

The rate at which the deposits from a dust cloud cover the surface of the ground can be found by summating the projected areas due to each grade in a manner similar to that used in Table 6.

5.3.1. *Uniform cubes.* The fraction of the surface covered by a deposit of uniform cubes is: Volume of the deposit ÷ Side of cube.

But if each cube were bisected by a horizontal plane and the top half removed the projected area of the lower halves would be the same but the volume of the deposit would be halved.

5.3.2. *Irregular particles of mixed sizes.* When irregular particles settle on the ground they come to rest with their major axes about horizontal so that they will cover a surface greater than cubes. A value for their shape factor could be found by performing an experiment to compare the area covered with that of cubes with equal falling speeds. In the absence of such experimental data the factor will be taken at 2 as for bisected cubes in 5.3.1.

Table 7 estimates the rate of coverage from the cloud of moderately irregular particles whose deposits were considered in Table 6.

TABLE 7. RATE OF COVERAGE ESTIMATED FOR CLOUD CONSIDERED IN TABLE 6

Grading of cloud sample			Rate of deposit (μ/day) (Taken from Table 6)	Rate of coverage (%/day) $\frac{200 \times \text{(Deposit in } \mu\text{/day)}}{\text{Mean size in microns (Taken from 5.3.1)}}$
Range of each grade	Mean size (μ)	% Within grade (%)		
106–76	91	5	0·079	0·173
76–53	65	15	0·153	0·480
53–37	45	35	0·185	0·822
37–27	32	30	0·087	0·633
27–19	23	10	0·014	0·122
<19	9·5	5	0·002	0·042
		100	0·530	2·272 (Mean 48 μ)

In grades less than 76 μ which fall more or less under streamline conditions:
Rate of coverage (% per day) = 0·528 × (diameter in microns) for ground concentrations of 1 mg/m³.

5.3.3. *Refraction with particles less than* 20 μ. H. E. Rose has pointed out that refractive effects magnify particles less than 20 μ so that their area can appear to be doubled in ranges of size less than 10 μ. The coverage from such fine fractions is slight, so that the error of ignoring refractive effects will be small, unless the suspension is unusually fine. Measurements carried out by light obscuration (cf. Appendix) automatically include the effects of shape and of refraction.

5.4 *Chart for calculations*

Fig. 5 gives formulae and graphs for estimating the deposits and coverages from

the properties of the suspended dust. In Table 8 it has been used for estimating the concentrations of dust in the atmosphere which just correspond to 100% cleanliness.

TABLE 8. CONCENTRATIONS WHICH CORRESPOND TO 100% CLEANLINESS

Description of surfaces	Rate of coverage for 100% cleanliness (%/day)	Mean diameter of deposited particles (μ)	Dust concentration (mg/m³)
Urban roads and pavements	0·02	5	0·0076
		50	0·00076
Rural grassland	0·2	5	0·076
		50	0·0076

Table 8 illustrates the manner in which Fig. 5 can be used and calls attention to the order of the atmospheric concentrations which would obtain in Britain if the above coverages were prevalent.

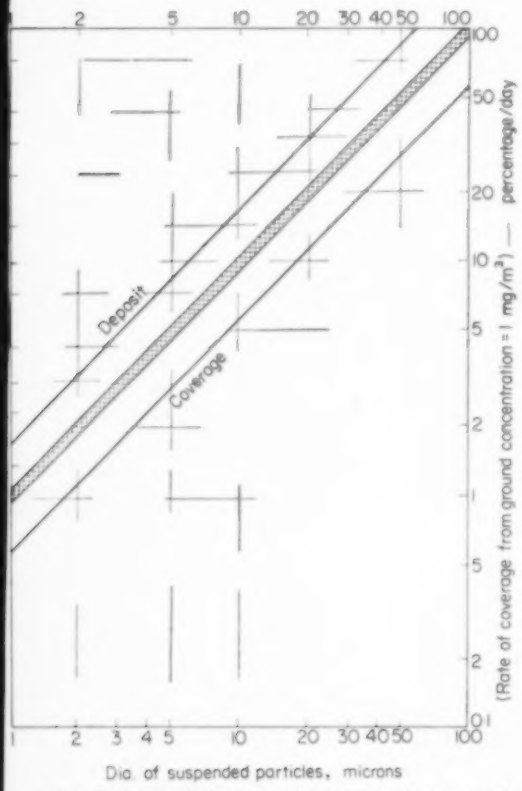

FIG. 5. Rates of deposit and coverage when ground concentration = 1 mg/m³ (Logarithmic scales).

RELEVANT FORMULAE

Size range	L.H. Scales Rate of deposit (μ/day)	R.H. Scales Rate of coverage (%/day)
All sizes	$13{\cdot}2 M_G \times F$	$\frac{200 \times \text{deposit } (\mu/\text{day})}{\text{mean dia. } (\mu)}$
<76 μ (approx.)	$26{\cdot}4 M_G \times \left(\frac{D}{100}\right)^2$	$0{\cdot}528\ M_G \times D$

Symbols referred to ground-level suspension:
D = Diameter (microns)
F = Falling speed (ft/sec)
M_G = Gravimetric concentration (mg/m³).

5.5 *Wind frequency and strength*

Many sites in Britain are surrounded by sources of dust whose emissions strongly influence the coverage which they receive. The long-term average rate can be predicted from field observations made during short periods of steady wind in each respective direction; it will be advisable to correct these:

(a) For the wind speed during the observation.
(b) For the wind frequency in the district averaged over several years (see Section 7 and Appendix).

6. OTHER OBSERVATIONS OF CLEANLINESS

The behaviour of atmospheric deposits which has been described is no more than a rational explanation of the commonly observed dinginess. Others have observed cleanliness in Britain and it remains to compare their results with coverages of equal alleged cleanliness; furthermore, the coverage to be expected from the dust discharged from our chimneys can be compared with the cleanliness in town and country. Although they start from quite different standpoints, Sections 6, 7 and 8 indicate that the results of these three examinations of cleanliness in Britain are not irreconcilable.

6.1 *Rates of deposit reported by D.S.I.R.*

The Department of Scientific and Industrial Research circulates monthly reports of the rates of deposit at about a hundred stations scattered over Britain; this work has continued for over 20 yr using a standard type of deposit gauge so that an enormous number of readings have been recorded. The principles of this system of measurement and its errors are discussed in the Appendix, from which it appears that there is no recognized method of interpreting the chaotic fluctuations in the observations. In an effort to introduce some order into this complex situation Table 9 follows a precedent of sorting the readings into groups according to generally observed standards of cleanliness associated with the activities of districts with different population densities.

The D.S.I.R. furnish no information about the size of the deposited dust; the estimates given in line 5 of the table are based on the types of emission and on the travel of the dust appropriate to each situation and upon experiences described in Section 7.

It is considered that the figures of percentage cleanliness given in line 7 do not conflict with the rather vague descriptions given in lines 1 and 3.

7. FIELD OBSERVATIONS OF COVERAGE

At a site near Northwich (Cheshire) during the spring and autumn of 1957 the writer made observations of the rate of coverage derived from sources of fine dust more than a mile distant. The deposits were collected by laying oiled plates on a flat expanse of grass for 2 or 3 hr of constant wind direction; they were then weighed in the laboratory and their projected area and height were measured from the obscuration of a parallel beam of light; the quotient of these two observations allows the mean height to be estimated (see Appendix). This operation is illustrated in Fig. 6. which includes a table of the principal results. It may be added that:

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TABLE 9. RÉSUMÉ OF D.S.I.R. DEPOSIT GAUGE RECORDS AND ESTIMATE OF CORRESPONDING COVERAGES

1. Description of locality		Country	Small towns	Highly industrialized	Remarks
2. Approximate density of population		<500 persons/mile^2	>2000 persons/mile^2	$>10{,}000$ persons/mile^2	
3. Standard of cleanliness		Desirable	Tolerated	Resented	
4. Observed rates of deposits in various units	(i) $\frac{\text{Tons}}{(\text{mile})^2\ 28\ \text{days}}$	0·77	7·7	77	$1 = 1\frac{\text{Ton}}{(\text{mile})^2\ 28\ \text{days}}$
	(ii) $\frac{\text{Tons}}{(\text{mile})^2\ \text{yr}}$	10	100	1000	$13{\cdot}02 = \frac{1\ \text{Ton}}{(\text{mile})^2\ 28\ \text{days}}$
	(iii) μ/day (sp. gr. = 2)	$0{\cdot}53 \times 10^{-2}$	$5{\cdot}3 \times 10^{-2}$	53×10^{-2}	$1 = \frac{145\ \text{Ton}}{(\text{mile})^2\ 28\ \text{days}}$
5. Approximate mean diameter of deposited particles (μ)		20	50	100	Although there are exceptions, e.g. soil raised from ploughed land by the wind, the more densely populated districts emit greater proportions of coarse dust, most of which will settle after travelling less than a mile.
6. Rate of coverage on earth surface		0·05%/day	0·2%/day	1%/day	$\%/\text{Day} = 200 \times \frac{\mu/\text{day (line 4 (iii))}}{\mu\ \text{diam. (line 5)}}$
7. Number of clean days in 10-day intervals between storms expressed as percentage of 10 days	*Pavements* Including allowance for dust bowl effects, smallest perceptible coverage = 0·2% earth's surface	40%	10%	2%	% clean days in 10 $= 10 \times \frac{(\text{Smallest perceptible coverage }\%)}{(\text{Daily coverage }\%)}$ % Cleanliness values greater than 100% are recorded as 100%.
	Grassland Smallest perceptible coverage = 2% of earth's surface	100%	100%	20%	

(1) In view of the considerable size of the deposits (mean dia. 34 μ), no correction has been applied for refractive magnification of fine particles.

(2) It is not practical to confine observations to days of average wind speed; since its speed will not influence the quantity of fine dust emitted from the sources the values recorded in the table are the observed coverage multiplied by a correction factor, namely (observed wind speed)/(average = 20 ft/sec).

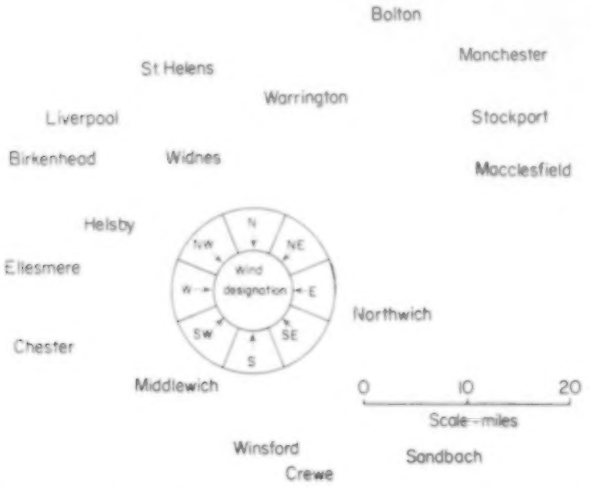


FIG. 6. Deposits of dust blown by wind from distant sources surrounding a site near Northwich.

COVERAGE AND SIZING OF THE DEPOSITS FROM EACH WIND

1	Wind designation	N	NE	E	SE	S	SW	W	NW	Remarks
2	Wind frequency (%)	6·6	6·1	8·0	12·2	20·0	14·1	17·6	15·4	Local 10 yr average
3	Possible sources of fine dust	Warrington	Macclesfield	Northwich	Crewe	Winsford	Chester	Ellesmere	Liverpool	See above
4	Observed coverage (%/day)	—	1	1·8	0·5	0·6	0·8	1·0	0·7	Corrected to average wind speed = 20 ft/sec
5	Observed mean diameter (μ)	—	32	22	32	42	34	40	30	Estimated from weight and line 4

Long-term averages coverage 0·8 %/day–diameter 34 μ.

7.1 *Comparison with appearance*

The mean coverage in the district is observed to be 0·8 per cent, so that the percentage cleanliness would be

$$\text{Grassland } 10 \times \frac{2{\cdot}0}{0{\cdot}8} = 25\%. \qquad \text{Pavements and roads } 10 \times \frac{0{\cdot}4}{0{\cdot}8} = 5\%.$$

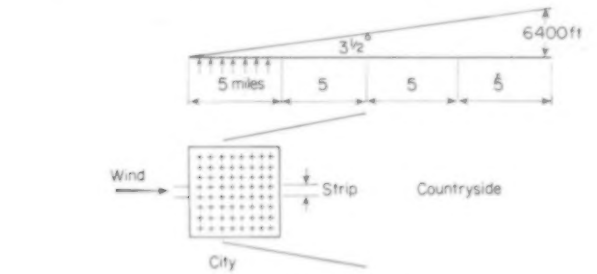
This is not inconsistent with a vague impression that built-up areas in the district appear dingy and the countryside markedly less so.

8. NATIONAL DUST NUISANCE

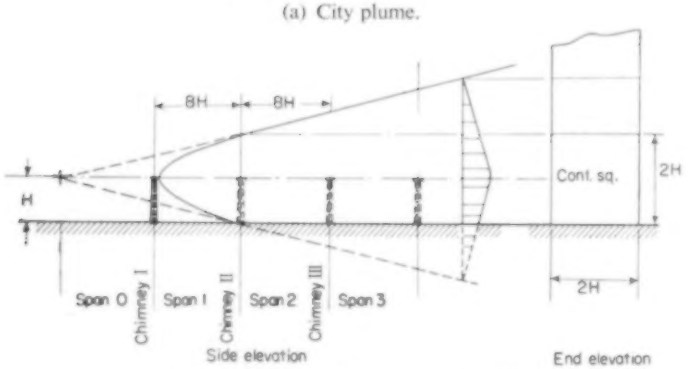
Combustion is widely accepted as the principal cause of the dust nuisance in this country; the amount of coal consumed in Britain is known accurately and permits the fine ash discharged to the atmosphere to be estimated roughly. The following sections trace a connexion between the coverage in town and country and their consumption of fuel.

8.1 *City dust emissions*

Fig. 7 (a) shows diagrammatically how smoke or fine dust mixes with the wind blowing over an extended source such as a large city. The wind blows continuously at its average speed (20 ft/sec) generating a plume shaped as a wedge inclined at $3\frac{1}{2}°$ to the horizon in average weather, but twice or half that angle under more extreme conditions. The city is some 5 miles square disposed symmetrically to the wind: there are numerous chimneys and the average strength of the emission is assumed to be in proportion to the density of the population. The ground concentrations in a centrally placed strip can be used to predict those in the city by assuming that only vertical spreading is important on account of the influence of the adjacent strips.



(a) City plume.



(b) Plume from multiple sources in strip.

FIG. 7. Dispersal of fine dust from cities.

8.1.1 *Single strip.* The side view of the strip of city in Fig. 7 (b) indicates numerous chimneys of height H spaced $8H$ apart so that smoke from No. 1 just spreads to the foot of No. 2 and so on; each $8H$ interval is called one span and bears a number 0–1, 2, etc. The wind is assumed to blow along the strip as between vertical walls of

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a canyon $2H$ wide, so that the smoke from each chimney spreads first so as to fill the contact square $2H \times 2H$ and then spreads vertically within the canyon.

First consider the spread of the smoke from a single chimney (I) at the left of span 1 when the others are shut off; the ground concentrations downwind from the single plume can be estimated by making the following approximations:

(i) *Dust distribution*

The concentration of dust in the undisturbed plume varies linearly between its fringes and a horizontal axial plane through the source in which the concentrations are twice the average in each cross-section normal to the wind.

(ii) *Shape of envelope*

In the first span the plume spreads roughly as a parabola from the top of a chimney height H to a square section $2H \times 2H$ called the contact square; the spread continues downwind in a wedge shape between the ground and the edge of the plume inclined at $3\frac{1}{2}°$ to the horizon.

(iii) *Effect of ground*

The ground concentrations are twice those which would obtain at the same level in an undisturbed plume.

A convenient method of making adjustments for the density of the population, wind speed, plume height, etc., is to express concentrations in the plume as multiples of the average concentration in the contact square $= C_S$; this would result from mixing the dust emitted from an area $8H \times 2H = 16H^2$ with the wind blowing through a square $4H^2$.

From the geometry of the triangular plume with an imaginary apex at the left of span O the following conditions obtain at the end of the Nth span:

Half-width of the undisturbed plume $= \left(\frac{N+1}{2}\right) H$

Height of the plume above the ground $= \left(\frac{N+3}{2}\right) H$

Mean concentration of the dust in the plume $= \frac{4H^2 C_S}{H\,[(N+3)/2] \times 2H} = \frac{4C_S}{N+3}$

$$\text{Ground concentration} = \begin{pmatrix}\text{Axial concentration in}\\ \text{undisturbed plume}\end{pmatrix} \times \left(1 - \frac{H}{(N+1)\,H/2}\right)$$

$$= 2 \times \frac{4H^2 C_S}{2[(N+1)\,H/2] \times 2H} \times \frac{N-1}{N+1}$$

$$= \frac{4C_S\,(N-1)}{(N+1)^2}$$

When N chimneys are in operation the mean concentration of dust in the plume at the end of the Nth span

$$= \frac{4NC_S}{N+3} = \frac{4C_S}{1+3/N} \to 4C_S \text{ when } N \text{ is large.}$$

And the ground concentration after N spans is the sum of those from a single source after 1–2, 3, ... N spans, viz.

$$\sum_{0}^{N} \frac{4C_S(N-1)}{(N+1)^2}$$

Values of the ground concentrations for various values of N have been estimated arithmetically and divided by the mean concentration to give the ratio:

(ground concentration)/(average for the plume);

these ratios have been plotted in Fig. 8 against a linear travel scale from 1 to 300 spans and against a logarithmic scale over 10 to 1000 spans. After the first few spans the plume average concentration will be about constant; the ground concentrations rise rapidly up to twice the plume average, more slowly to three times and then continue to rise gradually. Using a rather different approach LUCAS (1958) has obtained similar results and has suggested that H be taken as 30 ft, a value which has been used in Fig. 8 in preparing the lower scale of abscissae. It is unlikely that the local ground concentrations would be tolerated if the height of emission (H) were much less than 30 ft; it may be noted that, if the plume height were increased from 30 ft to 60 ft, the concentrations in the contact square and their pattern in each span would not change, but the length of the span would be doubled as would the travel for a given ground concentration.

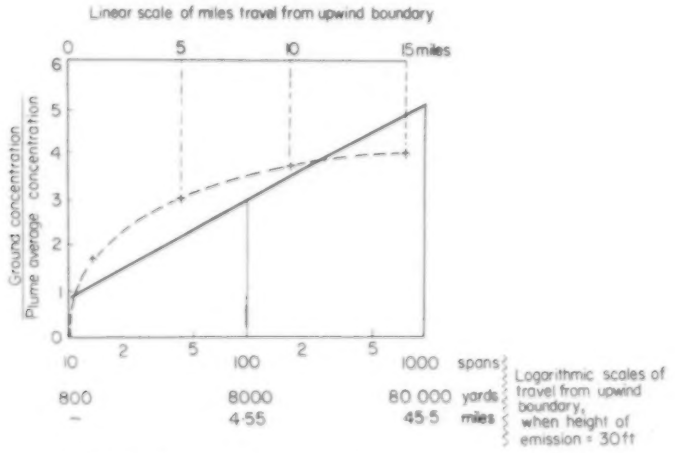

FIG. 8. City ground concentrations.

8.1.2 *Vertical dust distribution.* An extended source of dust affects the distribution of dust in the plume as well as its concentration at ground level. Consider that when dust is transferred from a uniform source the gradient of concentration would be uniform between the fringe of the plume and the ground if the resistance per unit height were uniform (see Fig. 9 (a)). However, the speeds of natural winds are least near the ground where the resistance is greatest so that dc/dh diminishes with height. As the plume travels downwind (Fig. 10 (b)) its depth becomes many times greater than the chimney height (30 ft) and:

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(a) The mean concentration approaches a limiting value.
(b) The overall resistance to transfer, the ground concentration and the ratio: (ground concentration)/(plume average) all continue to rise.

On the lee side of a city the plume will attain a height equal to about 1/16 of the span of the city; a further travel of one span downwind should suffice to convert even a highly inflected distribution to the linear configuration (Fig. 9 (c)) normally encountered in natural plumes under unsteady spreading conditions.

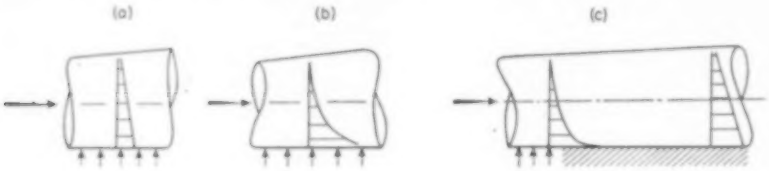
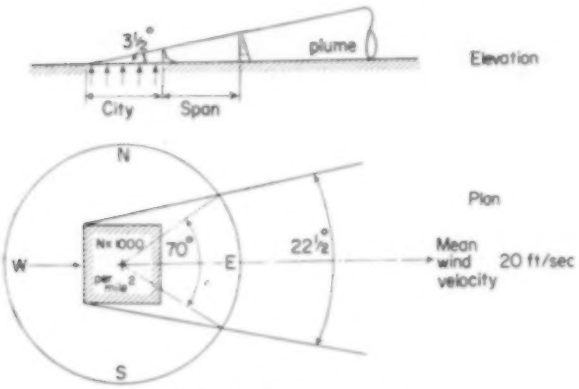
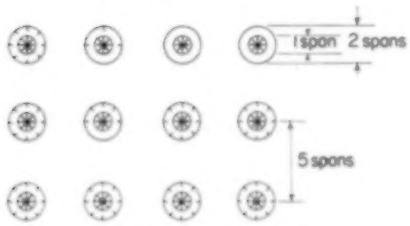


FIG. 9. Concentration gradients in city plumes.
(a) Plume with uniform resistivity.
(b) Natural plume.
(c) Change in concentration pattern on lee side.



(a) Single city in a desert.



(b) Uniform conurbation.

FIG. 10. Spread of city plumes.

8.1.3 *Dispersal of city plume in suburbs.* Metropolitan areas are surrounded by chimneys and experience the city plume in all wind directions; however, the suburbs are affected only when the wind is in an unfavourable quarter.

Fig. 10 considers how dust from a city spreads over a surrounding desert; the

dust is emitted uniformly from a square source orientated to the direction of the wind whose yawing action spreads the plume over an angle of about $\pi/8$.

Let C = Mean concentration of the dust in the plume over the city.
$\therefore$ $3C$ = Ground concentration in the city.

After travelling 1 city span downwind from the city the plume will have increased its width and its height so that mean concentration $= C/(2 \times 1{\cdot}4)$. During this travel the dust distribution will change from that of a continuous to that of a line source; the mean ground concentration over a 70° arc subtended at the centre of the city $= 2 \times C/(2 \times 1{\cdot}4) = C/1{\cdot}4$.

During a 100-day period of random wind the mean ground concentration over a 360° arc $= (C/1{\cdot}4) \times (70/360) = C/7{\cdot}2$.

$\therefore$ The ground concentrations in the city and 1 city span downwind are in the ratio $3 \times 7{\cdot}2 = 21{\cdot}6 : 1$.

Outside the city the mean concentration of the dust in the plume will vary as $(1/\text{Travel})^2$.

The 100-day average ground concentration at 2 city spans from its boundary, allowing for changes in wind direction = (city ground concentration)$/[21{\cdot}6 \times (2{\cdot}5/1{\cdot}5)^3]$ $\simeq$ 1 per cent of the city ground concentration.

In view of this rapid dilution the influence of sources whose strength is less than 100 times the mean will be negligible except in their immediate vicinity.

8.1.4 *Groups of cities.* The density of city populations is some twenty times the average for Britain, so it would appear that in a randomly orientated wind they will be surrounded by a polluted fringe whose radial depth $\simeq$ 1 city span. The city will not be an over-riding cause of visible deposits outside this fringe.

Groups of cities pitched less than three spans apart may be liable to the rise in ground concentration associated with very extensive sources. In addition the protagonists of green belts may consider that a separation of three spans between city centres does not provide sufficient unpolluted area. Table 10 indicates the relation between the separation between cities and the unpolluted fraction of the countryside.

TABLE 10

Pitch between city centres	3 Spans	4 Spans	5 Spans	6 Spans
Fraction of countryside unpolluted (%)	22	56	72	80
Fraction of countryside polluted (%)	78	44	28	20

8.2 *Average coverage in Britain*

The annual average consumption of coal in Britain is about 4 tons per head; it is estimated that 1 per cent of this is discharged to the atmosphere as fine ash particles less than 30 μ in size. Thus the activities of 1000 persons* disperse 4·6 kg/hr of fine

* Population densities are often reported in " thousands per square mile ".

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ash into the wind, as well as at least twice that amount of coarser dust which settles locally.

When a 20 ft/sec wind blows across an area 1 mile × 1 mile in area the volume of air polluted is $3{\cdot}5 \times 10^9$ m³/hr.

Mean concentration of 4·6 kg/hr of dust in the plume $= 1{\cdot}31 \times 10^{-3}$ mg/m³.

Ground concentration of fine dust less than 30 μ $= 3{\cdot}93 \times 10$ mg/m³.

Rate of growth of a deposited layer of 15 μ particles (average size) $= 2{\cdot}08 \times 10^{-3}$ μ/day.

$\therefore$ Coverage $= \dfrac{200 \times 2{\cdot}08 \times 10^{-3}}{15} = 0{\cdot}028\%$/day.

Owing to the magnification of fine particles by refraction the coverage will be about twice as great $= 0{\cdot}05\%$/day per 1000 persons per mile².

8.3 *Distribution of population and cleanliness*

8.3.1 *Town and country.* The proportionality between daily coverages and the density of population can be applied to simplified data about its distribution to form an impression of the cleanliness in town and in country.

TABLE 11. CLEANLINESS OF ENGLAND, WALES AND SCOTTISH LOWLANDS DERIVED FROM DENSITIES OF POPULATION

Description of district inhabited	Total number of inhabitants (millions)	Average span of inhabited units (miles)	Average density of populations (Persons/mile²)	Daily dust coverage (%)	% Clean days out of ten (%)
7 Conurbations; population over 1 million	20	18·5	8200	0·41	5
About 500 townships; average population 40,000 scattered about 12·5 miles apart	20	3·5	3300	0·16	12
Rural districts	10	—	150	0·0075	100
Totals	50	—	Average 650	0·032	100% on grassland 60% on built-up areas

The following comments amplify the information in Table 11:

(a) The distribution pattern of the urban population in Britain stems from the ancient market towns, usually 10–15 miles apart. The population has quadrupled

mainly by urban accretions since the eighteenth century; this has not caused townships to overlap their neighbours considerably: conurbations could be described as townships which have coalesced by growth.

(b) *Significance of N thousands per mile*^{2}. A density of 10,000 persons/mile^2 implies a reasonable standard of urban comfort; it is equivalent to 4 households each of 4 persons per acre; if two-thirds of the city is occupied by services other than housing, e.g. factories and shops, it is comparable with the council estate density of 12 houses/acre. There are areas of 1 mile^2 in many large towns in Britain which house up to 50,000 persons.

(c) *Interurban pollution.* The quoted densities of the populations of conurbations (London, Birmingham, Glasgow, etc.) include their suburban districts and imply that the whole area will appear dirty. The townships appear to be cleaner and their average spacing is 12·5 miles, so that there will be clean country between the smaller, but the polluted fringes of the larger will overlap.

The excess of their coverage over the average for the whole country	$=0{\cdot}16-0{\cdot}03$
	$=0{\cdot}13\%$ per day.
$\therefore$ Coverage at 1 span downwind $=0{\cdot}13/21{\cdot}6$	$=0{\cdot}006\%$ per day.

This would imply that the countryside between the smaller and more widely spaced towns is clean, e.g. in the North Riding of Yorkshire; it also explains the dirty appearance of so much of the West Riding countryside.

(d) *Large particles.* The ash content of coal is usually about 10 per cent, so that unless it is retained in the furnace or by dust catchers considerable amounts greater than 30 μ may be discharged to the atmosphere and reduce the cleanliness in cities below say 10 per cent; fractions of 1 clean day in 10 would be expected to exert no important influence on the public's impression of amenity.

It is unlikely that coverage is strictly proportional to rate of emission or to density of population. However, when coverages are predicted theoretically from densities of population in Table 11 the results agree with general impressions of cleanliness over a wide range of coverages, i.e. until more field measurements have been made it may be useful to use this approximation as a vehicle for discussing cleanliness; this follows a precedent set by LUCAS (1958) for discussing SO_2.

9. CONCLUSIONS

The dinginess experienced in Britain from deposits of dust is caused principally by burning coal. Chimneys all over the country emit fine and coarse dust which mixes with the wind and deposits on the ground according to its concentration and its grading: the coarse dust settles within a mile or two of its source, but the fines—less than 30 μ—mix with the wind rising to several thousand feet and are carried out to sea leaving a minute trail on the ground, which is particularly noticeable near large towns. Towns are populated about twenty times as densely as the countryside; the corresponding high ground concentration of dust is responsible for their dinginess.

It has been found that deposits which cover less than 0·4 per cent of the surface of roads or pavements are invisible. Violent rainstorms such as occur at intervals of about 10 days clean away previous deposits, so that if the average rate of coverage is less than 0·04 per cent per day there is rarely sufficient dust to be noticeable.

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Deposits on surfaces such as grassland are much less conspicuous than on roads or pavements, so that rural districts present a cleaner appearance. A rational measure of the cleanliness of a district is the fraction of a 10-day interval during which it appears clean: the fraction depends on the nature of the ground and the prevailing rates of coverage. Accordingly Table 12 sets out rates of coverage which correspond to 50% cleanliness in various sorts of districts because 50% is about the greatest fraction which the public are likely to tolerate as clean and the least which they can distinguish as dirty.

Table 12. Coverages likely to prove acceptable in certain environments

Situation	Surface	Rates of coverage corresponding to 50% cleanliness (%/day)
Towns subject to dust storms	Roads and pavements	0·04
	Grassland	0·20
Countryside free from re-entrainment	Roads and pavements	0·08
	Grassland	0·4

The rates of coverage given in Table 12 are the result of considering how re-entrainment and the terrain influence the optics of deposits of dust; the values agree reasonably with such general experiences as the time taken to foul sheets of paper exposed in towns or in the country.

Since a quantitative system of measuring cleanliness in terms of coverage constitutes a break with tradition, it is of interest to apply this new yardstick to conditions in Britain. Table 13 gives results of three different techniques which have been used to examine the cleanliness of situations in Britain for which there are data; it appears that:

(i) The deposits in cities greatly exceed the standards demanded by cleanliness; the same yardstick implies that the countryside is very clean.

(ii) There is accidental agreement between the two less reliable systems employed for estimating coverage (lines 1 and 3); both include numerous observations of a wide range of conditions, so that it would seem that:
  (a) Accurate measurements of coverage could be used to estimate cleanliness reliably.
  (b) In the absence of data on dust emission daily coverage can be predicted roughly from the density of the population.

(iii) The value of 0·8 per cent coverage per day reported from the Northwich area has been measured by a reliable system; a value of 0·2 per cent would be consistent with the other systems; the discrepancy might mean that the fuel consumption in the district and its fine ash content were both twice the national average; it indicates the importance of measurements at other sites.

Quite a small amount of field work, e.g. measurements of coverage and of the amount and grading of dust effluents would greatly assist the certainty of information on these questions. The techniques described in the Appendix could be applied to

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TABLE 13. SURVEY OF RATES OF COVERAGE AT VARIOUS SITUATIONS IN BRITAIN ESTIMATED BY THREE TECHNIQUES

Line	Col. I	Col. II	Col. III	Col. IV	Col. V	Col. VI	Col. VII
						Technique of measurement	
	Source	Situation	Country-side	Small towns	Highly industrialized	Description	Discussion of accuracy
1	Interpretation of D.S.I.R. Deposit Gauge Reports	Population per mile²	<500	>2000	>10,000	Dust collected in D.S.I.R. gauge during a week's exposure is weighed	No size analyses are reported. Weights may be under- or over-estimated by a factor of 2. An enormous volume of results are available
		% Daily coverage	0·05%	0·2%	1%		
2	Writer's observations in area near Northwich	Population of district	Residential area near Northwich (population ca. (2000/mile²)) but surrounded at each quarter by distant large cities or smaller ones within a few miles			Projected area of dust deposited during an hour on an oiled plate measured by light absorption	Limited number of results during three months; techniques of measurement reliable within ± 15%
		% Daily coverage	0·8%				
3	Estimates from density of population and fuel consumption	Population per mile²	<500	>2000	>10,000	Calculated from: (i) Density of population (ii) Fuel consumption per head (iii) Proportion of particles less than 30μ	The coverages seem likely to be under-estimated or over-estimated by a factor of 2
		% Daily coverage	0·02%	0·16%	0·5%		
4	% Daily coverage corresponding to 50% cleanliness (Table 12)		Grassland	Roads and pavements		For comparison with general observation	
			0·4%	0·04%	0·04%		
	Factor $\frac{\text{Approx. observed coverage}}{\text{Coverage for 50\% cleanliness}}$		$\frac{1}{10}$	5	20		

collect the necessary data, but some years may elapse before a useful body of results can be made available. Meanwhile it appears that the coverage theory agrees reasonably with the available observations of dinginess; it is suggested that the coverages given in Table 12 for 50 per cent coverage are an economical approach to cleanliness and are a standard suitable for estimating the efficiency of dedusting equipment because:

(a) They are derived from natural phenomena.
(b) They do not conflict seriously with other information.

Acknowledgement—The writer is indebted to Miss E. M. HALTON for her comments.

APPENDIX: MEASUREMENT OF COVERAGE

A.1 MECHANICS OF DEPOSITION

Consider the behaviour of fine atmospheric dust blown by the wind across a large flat expanse of grassland remote from chimneys or other large sources of dust emission. Near the surface of the grass there will be a streamline film a few millimetres deep, above which the air will flow in large turbulent eddies mixing the dust so that its concentration and grading will be virtually constant over distances of 100 yd. Normal suspensions of atmospheric dust are so dilute that the particles are over 100 diameters apart; collisions are rare and the rate of deposit on the ground

$$= (\text{Concentration above the film}) \times (\text{Falling speed of particles}).$$

When a small plate lies flat on the ground near the centre of a plot of flat grassland so that the wind blows over it without disturbance the plate will receive a representative deposit of dust. Fine dust deposited on dry smooth surfaces is liable to be re-entrained by the action of the wind and then to accumulate in hollows. Such accumulations become temporary sources if the wind freshens, and in this way can greatly magnify the atmospheric concentrations immediately in their lee. Accordingly the following precautions are advisable to reduce errors when using flat plates as instruments for measuring deposits of atmospheric dust:

(a) The plate is oiled or treated so as to prevent deposits from being re-entrained.
(b) To control disturbances of air flow and the influence of subsidiary dust sources there should be an expanse of level grass for about 30 yd upwind.

Experiment shows that when these precautions are followed the deposits on adjacent plates differ by less than 5 per cent; without precautions the errors can be large.

A.2 D.S.I.R. DEPOSIT GAUGE

This gauge is fully described in B.S. 1747 and has become so widely used that it is often regarded as the officially approved instrument. It was developed originally at the former Fuel Research Station and is now used by the D.S.I.R. for measuring the monthly rates of deposition at over a hundred stations in this country. It works on the principle of a rain gauge and is exposed to the atmosphere so that dust which settles in the upper tray is washed by the rain into a lower vessel from which the contents are removed at weekly or monthly intervals as is convenient for their evaluation in the laboratory. The instrument was originally intended for measuring monthly average rates of deposit in different districts; however, the results invariably include the influence of several wind changes so that it is very difficult to extend its function to correlating deposits to their sources. In addition the readings are subject to the following errors:

(a) About half the dust which enters the tray is liable to be re-entrained (LUCAS 1957).
(b) Often the weight of solid in solution in the rainwater is as great as the weight of the insoluble dust. The rainfall is usually about 10,000 times the dust fall so that this may be caused by fixation of SO_2 in raindrops, in which case the dissolved solids could be ignored (or corrected for small quantities of soluble dust); unfortunately, however, the proportion of the dissolved solids is neither constant nor predictable.
(c) As it flows across the upper tray the air-stream is subject to considerable disturbance which cannot be compensated easily.

If the errors due to (a) and (c) cancelled each other the uncertainty from (b) would still amount to a factor of about 2.

The D.S.I.R. gauge has been in service for over 20 yr collecting information in many countries; it is a valuable instrument for performing its original function: however, a need has now arisen for a deposit gauge which will estimate deposits accurately over a few hours, allowing the dust deposits from a plume to be related to the dust emitted from its source during a period in which the wind direction does not change.

A.3 FUNCTION OF SHORT-TERM DEPOSIT GAUGES

It may be reflected that the dust nuisance in Britain arises from sources so numerous and scattered that it is very helpful to eliminate the influence of wind change when observing the deposits from a single one of them; this can be carried out by measuring the deposits upwind and downwind during a few hours of steady wind so that the difference between the two plates can be ascribed to the source under examination, as in Fig. 11.

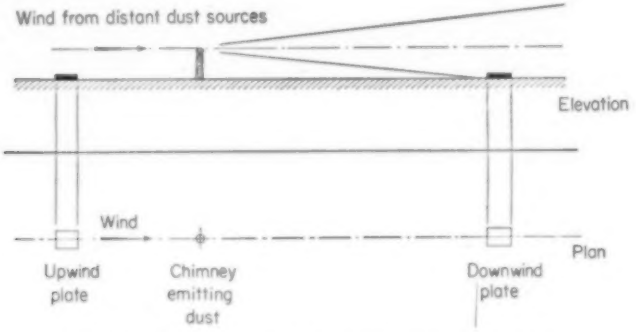

FIG. 11. Measurement of short-term rates of deposits

The advantages of this system can be illustrated by considering that the difficulties of analysing the results of deposits which have accumulated over a period such as a month are almost as great as attempting to allocate the responsibility for litter from the contents of a waste box.

A. 3.1 *Exposure of flat plate gauge*

A plate of opal Perspex 1 ft 0 in. wide × 2 ft 0 in. long with edges raised $\frac{1}{2}$ in. to prevent loss of dust by rainwater is covered with a transparent oil called Tellus and placed on a flat expanse of grass as described in A. 2. A 2 ft² plate exposed to a moderately dusty atmosphere should collect 5–50 mg of dust in about 2 hr.* The plate is then transferred to a container so that it can be removed to a laboratory where the volume of the deposit and the coverage can be estimated as described below.

A. 3.2 *Rate of coverage*

The percentage coverage per day to be expected in a given atmosphere can be measured very simply by exposing a white plate and observing the period of apparent cleanliness. For indoor dust a rubber bung is placed in the centre of a 6 in. filter paper; the coverage will then be 0·2 per cent when a clean circle can be seen upon removing the bung. The same system could be applied to outdoor dust, but a rainproof cover would be necessary.

A.4 MEASUREMENT OF RATE OF DEPOSIT AND OF COVERAGE AND MEAN DIAMETER

A. 4.1 *Surface measurement*

When a tray has been exposed to dust (Fig. 11) and is returned to the laboratory for evaluation it is subjected to the following operations:

(1) The dust and the oil are washed off the trays with petroleum ether into a beaker where the suspension settles for about 2 hr.

* An area of 2 ft² subject to a deposit = 1 μ/day receives a volume
$= 0{\cdot}775 \times 10^{-2}$ cm³/hr = 31 mg in 2 hr if $\sigma = 2$.

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(2) The clean supernatant liquor is syphoned off leaving a sediment of particles which are transferred to one of the glass cells in the modified Eel absorptiometer (Fig. 12).
(3) The fraction of light obscured from a parallel beam by the sediment is observed by setting the zero of the scale in accordance with the obscuration of a blank cell filled with syphoned liquor.

Notes

(a) *Modified Eel absorptiometer.* The standard Evans Electro-Selenium absorptiometer is a proprietary instrument for measuring the light opacity of solutions. It comprises a horizontal optical bench in which a parallel beam of light traverses the solution in a special glass cell so that the light intensity of the emergent beam can be observed by a P.E. cell. For measuring the opacity of rapidly settling suspensions the casing is tilted so that the light beam is vertical instead of horizontal and passes axially down the cross-section of a cylindrical cell about 1 cm diameter.*
(b) *Shape factor.* The projected area of a suspension scanned by a vertical beam will be practically the same as if the particles lay at rest on the ground.
(c) *Discoloration.* The opacity of the oil used for coating the gauges may be affected slightly by its exposure to the atmosphere. The P.E. cell reading can be compensated by using the clean liquor syphoned off both in the blank cell and for washing the sediment into the working cell.
(d) *Accuracy.* If the obscuration of light approaches 100 per cent the accuracy of the measurement will be improved by summating the surfaces found by evaluating fractions of the sample.
(e) *Rain.* Water will not mix with petroleum ether; if rain is likely to fall on the trays when exposed it may be advisable to smear them with a mixture of 15% acetone and 85% petroleum ether instead of 100% petroleum ether which is suitable for dry trays.

A. 4.2 *Evaluation of coverage*

Usually all the dust collected is washed into the cell for surface evaluation.

The coverage of dust on the tray

$$= [(\text{Observed fraction of light obscured}) \times (\text{Area of cell})] / \text{Area of tray } (2 \times 929 \text{ cm}^2).$$

A. 4.3 *Deposit*

The volume of the deposited solids can be estimated by evaporating the suspended fluid and weighing. When the sample available is insufficient for specific gravity measurement a value of 2·0 is often taken as a working assumption.

$$\text{Then the mean depth of the deposit in microns} = \frac{\text{Particle volume (cm}^3\text{)}}{\text{Tray area (cm}^2\text{)}} = \frac{\text{Volume (cm}^3\text{)}}{2 \times 929 \text{ (cm}^2\text{)}} \times 10^4 \, \mu.$$

A. 4.4 *Mean diameter of deposited particles*

In 5.3.1 it is considered that the mean height of the particles deposited on the tray can be taken as about one-half their mean diameter.

$$\text{Mean diameter} = \frac{2(\text{Deposit microns/day}) \times 100}{\% \text{ coverage/day}}.$$

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* Bottles of standard manufacture have been used.

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FIG. 12. Modified Eel absorptiometer in vertical position for surface measurements.

V
1959

Int. J. Air Poll. Pergamon Press 1959. Vol. 2, pp. 27–41. Printed in Great Britain

DIE AUSBREITUNG VON STAUB UND GAS NACH SUTTON

R. TRAPPENBERG
Meteorologischen Institut der Technischen Hochschule, Karlsruhe
(*Received* 27 *February* 1959)

Zusammenfassung—Die Berechnung der Immission aus der Emission eines Schlotes kann mit Hilfe der Gleichungen von SUTTON durchgeführt werden. Für die Praxis interessiert vor allem ein schneller Überblick über die zu erwartenden Gaskonzentrationen bzw. Staubniederschläge im Gebiet des Maximums. Da durch Windrichtungsänderungen die Immission immer über eine Fläche verteilt wird, haben wir die mittleren Konzentrationen bzw. Niederschläge in einem Rechteck von 1000×500 m² berechnet. Den Mittelpunkt dieses Rechtecks bildet der theoretische Maximumspunkt, die längere Seite liegt in Windrichtung.

Wir variierten in der Berechnung die Parameter Windgeschwindigkeit v, meteorologischer Koeffizient n und spezieller Austauschkoeffizient C_z. Konstant blieb der Wert des Koeffizienten C_y mit 0,1 [cm$^{n/2}$] und der Auswurf mit 100 [g/sec].

Die Mittel- und Grenzwerte der Gaskonzentrationen in Abhängigkeit von den Kaminhöhen sind in den Abbildungen 1–4 für die Windgeschwindigkeiten 2 bis 8 [m/sec] zusammengefaßt. Die dazugehörigen Entfernungen der theoretischen Maximumspunkte vom Schlot in Windrichtung enthält die Tabelle 2.

Für die Staubniederschläge sind die Ergebnisse in den Tabellen 3–6 in Abhängigkeit von den meteorologischen Werten und der Kaminhöhe zusammengestellt. Tabelle 7 gibt die Entfernungen des theoretischen Maximumspunktes vom Schlot.

Für von 100 [g/sec] abweichenden Emissionen sind die angegebenen Immissionswerte mit dem hundertsten Teil des tatsächlichen Auswurfs ($Q/100$) zu multiplizieren, da die Immissionen proportional den Emissionen sind.

Wenn C_y Werte annimmt, die von 0,1 [cm$^{n/2}$] verschieden sind, dann sind die Korrekturen nach Tabelle 1 anzubringen, die für das Verhältnis C_y/C_z berechnet wurden.

Die Korrekturfaktoren für die mittleren Windrichtungsschwankungen in Strich der 32-teiligen Richtungsskala wurden in Abhängigkeit von der Entfernung des Maximumspunktes vom Schlot berechnet (Abb. 6).

Aus den Tabellen und Abbildungen ist die Abschätzung der voraussichtlichen Immission bei gegebener Emission eines Industriewerkes möglich, sofern die Windgeschwindigkeit und ihre Änderung mit der Höhe, die Windrichtung und ihre Schwankung und die Regenintensität mit Andauer und Häufigkeit bekannt sind. Vergleiche zwischen berechnetem und gemessenem Staubniederschlag von DIEM ergaben zufriedenstellende Übereinstimmung. Eine gleichartige Prüfung der Gas- oder Staubkonzentration konnte noch nicht durchgeführt werden, wäre aber zur Sicherung der Ergebnisse dringend notwendig.

Abstract—It is possible to calculate the pollution caused by emission from a chimney by means of SUTTON's equations. For practical purposes, it is mainly desirable to estimate what the concentration of gases and deposition of dust will be in the region of the maximum. As the direction of wind is variable and the pollution therefore distributed over an area, we have calculated the mean concentration of gas and deposition of dust over an area of 1000 by 500 m². The theoretical maximum point is in the centre of this rectangle and the longer side is parallel to the wind direction.

In the calculations the following parameters were varied: wind velocity v, meteorological coefficient n and specific exchange coefficient C_z. Constant values were used for the coefficient C_y at 0·1 (cm$^{n/2}$) and for the chimney discharge at 100 g/sec.

Figs. 1 to 4 show mean and limiting values of flue-gas concentrations as function of height of

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chimney for wind velocities between 2 and 8 m/sec. The corresponding distances of the pollution maximum from the chimney in the wind direction are shown in Table 2.

The results for dust deposition as function of meteorological conditions and height of chimney are given in Tables 3 to 6, while Table 7 shows the distances between the theoretical maximum point and the chimney.

If the dust emission Q differs from 100 g/sec the deposition values given in Tables 3 to 6 must be multiplied by $Q/100$, as dust deposition (immission) is proportional to emission. If the value of C_y differs from 0·1 $cm^{n/2}$, a correction must be used according to Table 1 which shows the ratio C_y/C_z. Correction factors for the variation of mean wind direction on a scale with 32 divisions were calculated as function of the distance between chimney and pollution maximum (Fig. 6).

From the tables and figures given it is possible to estimate the pollution to be expected from an industrial plant with a known emission provided the following factors are known: the wind speed and its variation with height, the wind direction and its range, the frequency, duration and amount of rainfall. A comparison of the calculated dust deposition with that measured by DIEM gave satisfactory agreement. Similar tests of gas and airborne dust concentration have not as yet been carried out, but there is a need to make such tests in order to confirm the calculated results.

1. EINLEITUNG

DIE Bestimmung der Immission aus der Emission wird für alle Neuplanungen von staub- und abgaserzeugenden Betrieben von immer grösserer Bedeutung, soll nicht überraschend eine starke Belästigung des Menschen in der Umgebung dieser Werke durch den Staubauswurf oder eine Schädigung an Pflanzen durch toxisch wirksame Gaskonzentrationen eintreten. Die Emission muss deshalb derart begrenzt werden, dass unzuträgliche Konzentrationen oder Staubniederschläge nicht oder wenigstens nur in sehr seltenen, extremen Ausnahmefällen erreicht werden können. Damit ist die Möglichkeit gegeben, die Industrie für den Normal- und Extremfall zu beraten und entsprechende Sicherheitsmaßnahmen zu treffen.

Um die Möglichkeiten abzuschätzen, ist die Kenntnis des Zusammenhanges zwischen Emission und Immission notwendig, deren quantitative Berechnung unter Berücksichtigung verschiedener Zustände der Luft nach den Formeln von SUTTON (1947) möglich ist. Diese ergeben, wie alle bisherigen Anwendungen zeigen, die derzeit beste mathematische Verknüpfung von Immission und Emission.

2. GRUNDLAGEN DER BERECHNUNG

SUTTON (1947) findet für den Zusammenhang zwischen der Emission Q und der Immission K:

$$K=\frac{Q}{\pi C_y C_z v x^{2-n}} \cdot \exp\left(\frac{-y^2}{C_y^2 x^{2-n}}\right)\left[\exp\left(\frac{-(z-h)^2}{C_z^2 x^{2-n}}\right)+\exp\left(\frac{-(z+h)^2}{C_z^2 x^{2-n}}\right)\right] \qquad (1)$$

Dabei bedeuten:

- C spezieller Austauschkoeffizient nach SUTTON [$cm^{n/2}$]
- h Höhe der Staubquelle [cm]
- K Gaskonzentration [g/cm^3]
- n meteorologischer Exponent
- Q Staubauswurf [g/sec]
- S Staubniederschlag [g/cm^2 sec]
- v Windgeschwindigkeit [cm/sec]
- x horizontale Achse in Windrichtung [cm]
- y horizontale Achse senkrecht zur Windrichtung [cm]
- z vertikale Achse senkrecht zur Windrichtung [cm]

} Rechts-system

Mit Hilfe dieser Gleichung kann man unter bestimmten Annahmen für die durch die meteorologischen Bedingungen festgelegten Größen n, C_z, C_y die Verteilung der Konzentration eines Gases berechnen. Dies ergibt am Boden Linien gleicher Konzentration, wie sie DIEM (1951) zuerst gezeich-

net hat. Aus der Gleichung (1) berechnet sich ein bestimmter Punkt der maximalen Gaskonzentration in der Entfernung x_{max}

$$x_{max} = \left(\frac{h}{C_z}\right)^{2/(2-n)} \tag{2}$$

wobei die Höhe der Konzentration

$$K_{max} = \frac{2Q}{e\pi v h^2} \cdot \frac{C_z}{C_y} \tag{3}$$

beträgt.

Dieser Wert K_{max} wird sich aber nur einstellen, wenn die seitliche Ausbreitung (in y-Richtungen) der Rauchfahne einzig von dem Austauschkoeffizienten C_y bestimmt wird. Richtungsschwankungen durch Turbulenzelemente, die im Verhältnis zu den Dimensionen eines Rauchstoßes groß sind, werden dabei nicht berücksichtigt. Diese Richtungsschwankungen des Windes werden das Bild der Linien gleichen Gasgehaltes stets verzerren, insbesondere wird man nie einen Punkt, sondern stets eine Fläche maximaler Konzentration erhalten. Auf Grund theoretischer Erwägungen und Messungen (DIEM, 1956; DIEM, 1957; DIEM, 1958) sind wir deshalb dazu übergegangen, die maximale mittlere Konzentration für ein Normrechteck zu berechnen, dessen Mittelpunkt im theoretischen Maximumspunkt liegt und dessen Länge in Windrichtung (in x-Richtung) $2x_0 = 1000$ m, dessen Breite (in y-Richtung) $2y_0 = 500$ m beträgt. Wir bestimmten also nicht K_{max}, dessen Angabe höchstens für sehr kurze Zeiten gelten kann, sondern eine maximale mittlere Konzentration.

$$K = \frac{\displaystyle\int_{-y_0}^{y_0}\int_{x_1}^{x_2} K\,dx\,dy \qquad x_1 = x_{max} - x_0}{\displaystyle\int_{-y_0}^{y_0}\int_{x_1}^{x_2} dx\,dy \qquad x_2 = x_{max} + x_0} \tag{4}$$

Der Zähler der rechten Seite ergibt sich dabei aus Gleichung (1) zu:

$$\int_{-y_0}^{y_0}\int_{x_1}^{x_2} K\,dx\,dy = \frac{4}{2-n} \cdot \frac{Q}{\sqrt{\pi}} \cdot \frac{h^{n/(2-n)}}{vC_z^{2/(2-n)}} \cdot \Phi\left(\frac{y_0}{C_y x_{max}^{(2-n)/2}}\right) \int_{u_2}^{u_1} \frac{e^{-u^2}}{u^{2/(2-n)}}\,du \tag{5}$$

$$u_1 = \frac{1}{\left(1 - \dfrac{x_0}{x_{max}}\right)^{(2-n)/2}} \qquad u_2 = \frac{1}{\left(1 + \dfrac{x_0}{x_{max}}\right)^{(2-n)/2}}$$

Dabei ist vor der Integration über x der Mittelwertsatz angewendet und wie von uns schon früher berechnet (DIEM und TRAPPENBERG, 1957) in Φ $x = x_{max}$ gesetzt worden. Der Fehler bleibt dadurch unter 1/2 Prozent.

Analog wird der Staubniederschlag berechnet. Dieser ergibt sich am Boden nach TRAPPENBERG (1957a) mit Hilfe der Gleichung (1) zu

$$S = \frac{0{,}6 \cdot Q \cdot (2-n) \cdot h \cdot v^{1-n}}{\pi C_y C_z x^{2(2-n)} \left|\dfrac{dv}{dz}\right|_{z=0}^{1-n}} \cdot \exp\left(-\frac{y^2}{C_y^2 x^{2-n}}\right) \cdot \exp\left(-\frac{h^2}{C_z^2 x^{2-n}}\right) \tag{6}$$

Daraus ergibt sich ein punktförmiges Maximum in der Entfernung:

$$x_{max} = \left(\frac{h^2}{2C_z^2}\right)^{1/(2-n)} \tag{7}$$

und die Menge des Staubniederschlages

$$S_{max} = \frac{0{,}6 \cdot 4 \cdot Q \cdot (2-n) \cdot v^{1-n}}{e^2 \pi h^3 \left|\dfrac{dv}{dz}\right|_{z=0}^{1-n}} \cdot \frac{C_z^3}{C_y} \tag{8}$$

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Analog zu den Überlegungen bei der Konzentration wird wieder das Mittel über das Normrechteck gebildet.

$$\bar{S} = \frac{\displaystyle\int_{-y_0}^{y_0}\int_{x_1}^{x_2} S\,dx\,dy \qquad x_1 = x_{\max} - x_0}{\displaystyle\int_{-y_0}^{y_0}\int_{x_1}^{x_2} dx\,dy \qquad x_2 = x_{\max} + x_0} \tag{9}$$

Der Zähler ist nach Ausführung der Integration:

$$\int_{-y_0}^{y_0}\int_{x_1}^{x_2} S\,dx\,dy = \frac{1{,}2}{\sqrt{\pi}} \cdot \frac{Q \cdot v^{1-n}}{\left(\frac{h}{C_z}\right)^{2(1-n)/(2-n)} \left|\frac{dv}{dz}\right|^{1-n}} \cdot \Phi\left(\frac{y_0}{C_y x_{\max}^{(2-n)/2}}\right) \cdot \int_{u_1}^{u_2} e^{-u^2} \cdot u^{2(1-n)/(2-n)}\,du \tag{10}$$

$$u_1 = \frac{\sqrt{2}}{\left(1 + \frac{x_0}{x_{\max}}\right)^{(2-n)/2}} \qquad u_2 = \frac{\sqrt{2}}{\left(1 - \frac{x_0}{x_{\max}}\right)^{(2-n)/2}}$$

3. AUSRECHNUNG

Mit den Gleichungen (4) und (9) werden die mittleren Konzentrationen bezw. Staubniederschläge über dem Normrechteck berechnet. Dabei sind bestimmte Werte für die meteorologischen Faktoren vorzugeben.

Bei unseren Messungen, deren Veröffentlichung vorbereitet wird, fanden wir große Schwankungen des meteorologischen Exponenten n (zwischen – 10 und 1,5) und des speziellen Austauschkoeffizienten C_z (zwischen 0 und 0,7 [cm$^{n/2}$] (DIEM, 1956; TRAPPENBERG, 1957a; TRAPPENBERG, 1957b).

Wir benutzen in dieser Arbeit die am häufigsten vorkommenden Werte dieser Koeffizienten und erweiterten damit die früheren Arbeiten von DIEM und TRAPPENBERG (1953) und DIEM und TRAPPENBERG (1957). Es werden verwendet für den meteorologischen Exponenten n:

$$n = 0{,}1 \quad 0{,}2 \quad 0{,}3 \quad 0{,}4 \quad 0{,}5 \quad 0{,}6$$

für den speziellen Austauschkoeffizienten C_z:

$$C_z = 0{,}05 \quad 0{,}10 \quad 0{,}15 \quad 0{,}20 \quad 0{,}25 \quad 0{,}30$$
$$0{,}40 \quad 0{,}50 \quad 0{,}60 \text{ [cm}^{n/2}\text{]}$$

für den Koeffizienten C_y:

$$C_y = 0{,}1 \text{ [cm}^{n/2}\text{]}$$

für die Windgeschwindigkeit:

$$v = 2,\ 4,\ 6,\ 8 \text{ [m/sec]}$$

und wir berechneten aus allen Variationen dieser Größen die mittlere Konzentration K bezw. den mittleren Staubniederschlag S für die Kaminhöhen:

$$h = 20,\ 40,\ 60,\ 80,\ 100,\ 120 \text{ m}$$

Dabei wurde der Auswurf $Q_1 = 100$ [g/sec] gesetzt. Da sowohl K wie S proportional Q sind, ergeben sich diese beiden Größen für $Q \neq 100$ [g/sec] durch eine einfache Multiplikation mit

$$\frac{Q}{Q_1} = \frac{Q}{100}$$

Eine Korrektion für einen anderen C_y—Wert als 0,1 ist auch noch nachträglich an den berechneten Werten von K und S möglich, da C_y nur in den Faktor Φ in den Gleichungen (5) bezw. (10) eingeht.

Wir können den Argumentwert von Φ unschreiben, wodurch wir erhalten:
für die Konzentration

$$\frac{y_0}{C_y}\cdot\frac{1}{x_{\max}^{(2-n)/2}}=\frac{y_0}{h}\cdot\frac{1}{C_y/C_z}$$

für den Niederschlag

$$\frac{y_0}{C_y}\cdot\frac{1}{x_{\max}^{(2-n)/2}}=\frac{y_0}{h}\cdot\frac{\sqrt{2}}{C_y/C_z}$$

Damit hängt Φ von der Kaminhöhe h und dem Verhältnis C_y/C_z ab. Ist dieses Verhältnis $C_y/C_z\leqslant 1$ so können wir $\Phi=1{,}00$ setzen. Wir müssen deshalb Φ nur berücksichtigen im Fall $C_y=0{,}10$ und $C_z=0{,}05$.

Für alle Fälle $C_y>0{,}1$ geben wir in Tabelle 1 in Abhängigkeit von der Kaminhöhe h und dem Verhältnis C_y/C_z einen Korrekturfaktor, der an den Ergebnissen der Rezhnungen (Gleichungen (4) bzw. (9)) anzubringen ist.

TABELLE 1. KORREKTURFAKTOREN FÜR $C_y\neq 0{,}1$

	$C_y/C_z=8$		$C_y/C_z=4$		$C_y/C_z=2$	
h [m]	für K	für S	für K	für S	für K	für S
20	0,97	1,00	1,00	1,00	1,00	1,00
40	0,73	0,88	0,97	1,00	1,00	1,00
60	0,54	0,71	0,86	0,96	1,00	1,00
80	0,43	0,56	0,75	0,88	1,00	1,00
100	0,36	0,47	0,66	0,79	0,99	0,99
120	0,33	0,44	0,61	0,71	0,97	0,98

Für $C_y/C_z\leqslant 1$ wird der Korrekturfaktor 1,00

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Die Durchrechnung aller Werte erfolgte einschließlich der notwendigen Integrationen numerisch mit Hilfe von Rechenmaschinen.

4. DARSTELLUNG DER ERGEBNISSE

Die Ergebnisse der Rechnung sind für die Konzentrationen in den Abb. 1–5 und Tabelle 2, für den Staubniederschlag in den Tabellen 3–7 dargestellt.

(*a*) *Konzentration*

Die Schwankung der Konzentration mit der Windgeschwindigkeit als Parameter ist bei den vorgegebenen meteorologischen Daten für n, C_z und C_y gering. Wir fassen deshalb—einem Vorschlag von Dangl folgend—für die Windgeschwindigkeiten 2, 4, 6, 8 m/sec sämtliche Werte in einem Bild zusammen. (Abb. 1–4.)

In den Abb. 1–4 ist als Abszisse die Kaminhöhe h in [m], als Ordinate die Konzentration in [mg/m³] aufgetragen. Die gestrichelten Kurven geben jeweils die Begrenzung aller von uns berechneten Konzentrationen für einen Auswurf von 100 g/sec. Die ausgezogene Kurve ist das Mittel der Einhüllenden. Diese Mittelkurven haben wir zum besseren Vergleich in Abb. 5 zusammengefasst. Als zusätzliche Kurve wurde dabei gestrichelt die Abweichung der Konzentration der Einhüllenden von den jeweiligen mittleren Konzentrationen in Prozent angegeben. Für diese Kurve gilt als Ordinate die Prozentteilung rechts. Da bei den größeren Kaminhöhen der Absolutwert gering wird, spielt die Abweichung von 50 Prozent keine Rolle. Allgemein ist aus den Kurven zu erkennen, dass eine Erhöhung des Kamins von 20 auf 40 m Höhe

einen Abfall der Konzentration auf die Hälfte bringt. Bei einer Erhöhung des Schlotes um 20 m bei 100 m Kaminhöhe ist der Abfall der Konzentration nur noch gering. Dies gilt insbesondere bei höheren Windgeschwindigkeiten, wobei die Schlothöhe in ebenem unbebautem Gelände gemessen ist. Welche effektiven Kaminhöhen bei Berücksichtigung der Orographie eingesetzt werden müssen, kann nur von Fall zu Fall entschieden werden (DIEM, 1957; DIEM, 1958).

Wir kommen mit dieser Berechnung zu dem zunächst überraschenden Ergebnis, dass für die Gaskonzentration nur die Kaminhöhe und die Windgeschwindigkeit wesentlich sind. Die sonstigen atmosphärischen Verhältnisse—vor allem der meteorologische Exponent n—beeinflussen lediglich die Entfernung des Maximums.

In diesen Kurven ist die Entfernung des Maximums der Konzentration nicht enthalten, weil deren Schwankung in Abhängigkeit von den meteorologischen Faktoren groß ist. Aus Tabelle 2 ist bei gegebenem n- und C_z—Wert diese Entfernung abzulesen. Entfernungen unter 0,5 km sind nicht aufgeführt, da dann die Berechnung der Konzentration bezw. des Niederschlages unterblieb. Einmal konnte bei diesen Entfernungen das Normrechteck von 500 × 1000 m nicht mehr verwendet werden, zum anderen spielt die lokale Strömung im Nahbereich des Werkes nach IBING (1954) eine derart grosse Rolle, dass unsere Rechnung nicht mehr voll gültig sein kann.

(*b*) *Staubniederschlag*

Die Werte des Staubniederschlages ändern sich mit den meteorologischen Faktoren stärker als die Konzentration, wie aus den Messergebnissen DIEM (1956), DIEM (1957), DIEM (1958) zu erwarten war; sie wurden für einen Auswurf von 100 g/sec berechnet. Wir stellten das Ergebnis der Berechnung in den Tabellen 3–6 zusammen, wobei jeweils für eine Windgeschwindigkeit eine Tabelle mit der Kombination der anderen Parameter berechnet wurde. Aus den Tabellen geht hervor, dass neben der Windgeschwindigkeit es vor allem der meteorologische Exponent n ist, der die Menge des Staubniederschlages zusätzlich bestimmt. Die Entfernung des Maximums wieder ist in Tabelle 7 analog zur Tabelle 2 zusammengestellt.

Eine Überprüfung durch einen Vergleich zwischen Berechnung und Messung konnte DIEM (1956), DIEM (1957) durchführen.

Die Ergebnisse zeigen, dass man bei sorgfältiger Anwendung der Berechnung gute Übereinstimmung erhält. Voraussetzung ist dabei, dass der Anteil der Windrichtung, ihre Schwankung und der Einfluß des Regen- (bezw. Schnee-) Niederschlages berücksichtigt wird [DIEM, 1956; DIEM, 1957; DIEM, 1958]. Eine erste quantitative Rechnung über den Einfluß des Regens auf die Auswaschung von Teilchen aus der Luft gab DIEM (1951).

Die Berücksichtigung der Schwankung der Windrichtung erfolgt nach von DIEM und TRAPPENBERG (1957) abgeleiteten Gleichungen, wobei wir unter " Schwankung " die Richtungsänderungen verstehen, die sich aus der 5- oder 10-minütlichen Registrierung ergeben. Die Gleichungen ergeben einen von der Entfernung der maximalen Konzentration bezw. des Staubniederschlages abhängigen Korrekturfaktor F, der aus Abb. 6 zu entnehmen ist. Dabei ist der Parameter die Schwankung der Windrichtung in Strich (1 Strich $\cong 1/32$ der Windrose $= 11{,}25°$). Mit diesem Faktor sind unter Berücksichtigung des jeweiligen x_{max} die aus den Abb. 1–4 bezw. Tabellen 3–6 entnommenen Werte zu multiplizieren, um den zutreffenden Wert der Gaskonzentration bezw. des Staubniederschlages zu erhalten.

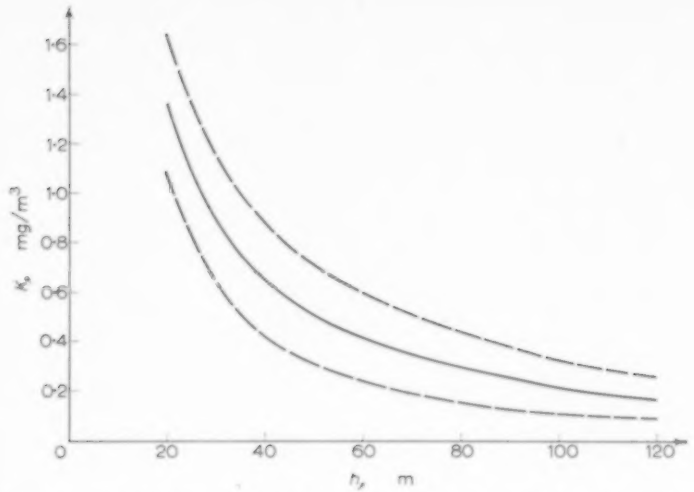

Abb. 1. Maximale mittlere Konzentration [mg/m³] bei der Windgeschwindigkeit $v=2$[m/sec] und $n=0{,}1 \ldots 0{,}6 \quad C_z=0{,}05 \ldots 0{,}60$ [cm$^{n/2}$].

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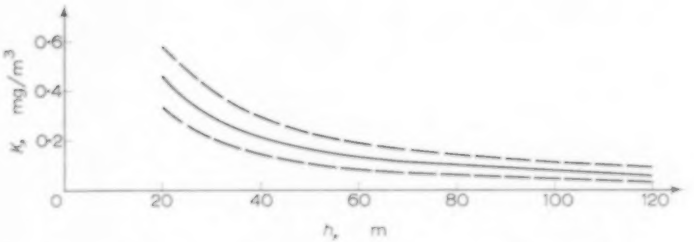

Abb. 2. Maximale mittlere Konzentration [mg/m³] bei der Windgeschwindigkeit $v=4$[m/sec] und $n=0{,}1 \ldots 0{,}6 \quad C_z=0{,}05 \ldots 0{,}60$ [cm$^{n/2}$].

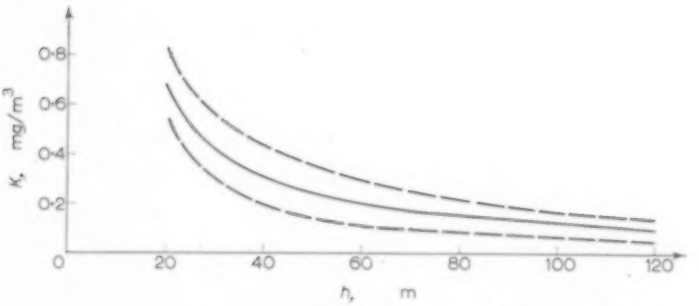

Abb. 3. Maximale mittlere Konzentration [mg/m³] bei der Windgeschwindigkeit $v=6$[m/sec] und $n=0{,}1 \ldots 0{,}6 \quad C_z=0{,}05 \ldots 0{,}60$ [cm$^{n/2}$].

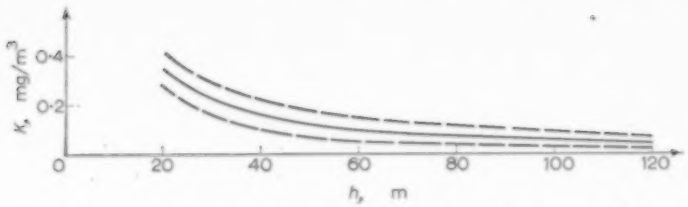

ABB. 4. Maximale mittiere Konzentration [mg/m³] bei der Windgeschwindigkeit $v=8$[m/sec] und $n=0{,}1 \ldots 0{,}6$ $C_z=0{,}05 \ldots 0{,}60$ [cm$^{n/2}$].

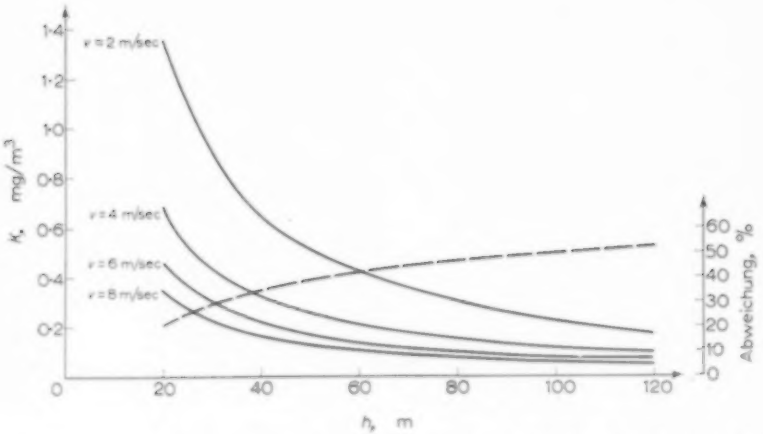

ABB. 5. Mittel der maximalen mittleren Konzentrationen [mg/m³] bei $v=2 \ldots 8$[m/sec], $n=0{,}1 \ldots 0{,}6$ $C_z=0{,}05 \ldots 0{,}60$ [cm$^{n/2}$].

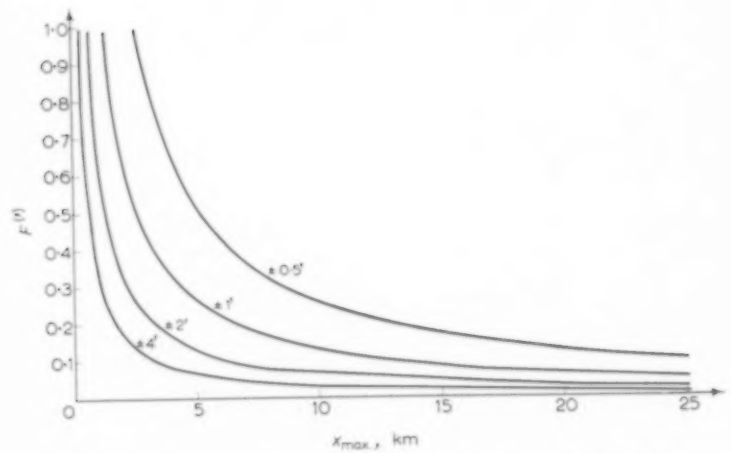

ABB. 6. Verkleinerungsfaktor F' wegen der Schwankung der Windrichtung.

TABELLE 2. ENTFERNUNGEN DER MAXIMALEN KONZENTRATIONEN (in km)

		Höhe [m]										
n	C_z[cm$^{n/2}$]	20	30	40	50	60	70	80	90	100	110	120
0,1	0,05	0,7	1,1	1,4	1,8	2,2	2,6	3,0	3,4	3,8	4,2	4,6
	10		0,5	0,7	0,9	1,1	1,3	1,4	1,6	1,8	2,0	2,2
	15			0,5	0,6	0,7	0,8	1,0	1,1	1,2	1,3	1,4
	20					0,5	0,6	0,7	0,8	0,9	1,0	1,1
	25						0,5	0,6	0,6	0,7	0,8	0,9
	30							0,5	0,5	0,6	0,6	0,7
	40										0,5	0,5
	50											
	60											
0,2	0,05	1,3	2,0	2,8	3,6	4,4	5,2	6,0	6,9	7,8	8,7	9,6
	10	0,6	0,9	1,3	1,6	2,0	2,4	2,8	3,2	3,6	4,0	4,4
	15		0,6	0,9	1,0	1,2	1,5	1,8	2,1	2,4	2,6	2,8
	20			0,6	0,8	0,9	1,1	1,3	1,5	1,7	1,9	2,1
	25			0,5	0,6	0,7	0,9	1,0	1,2	1,3	1,5	1,6
	30				0,6	0,7	0,8	0,9	1,0	1,1	1,2	1,3
	40						0,5	0,6	0,7	0,7	0,8	0,9
	50							0,5	0,5	0,6	0,7	0,7
	60									0,5	0,5	0,6
0,3	0,05	2,6	4,2	5,9	7,7	9,5	11,3	13,2	15,2	17,2	19,2	21,3
	10	1,2	1,9	2,6	3,3	4,1	5,0	5,9	6,8	7,6	8,6	9,3
	15	0,7	1,1	1,6	2,1	2,6	3,1	3,6	4,2	4,7	5,3	5,9
	20	0,5	0,8	1,1	1,5	1,8	2,2	2,6	3,0	3,4	3,8	4,2
	25		0,6	0,9	1,2	1,4	1,7	2,0	2,3	2,6	2,9	3,2
	30		0,5	0,7	0,9	1,2	1,4	1,6	1,8	2,1	2,4	2,6
	40			0,5	0,7	0,8	1,0	1,2	1,4	1,5	1,7	1,8
	50				0,5	0,6	0,8	0,9	1,1	1,2	1,3	1,4
	60					0,5	0,6	0,7	0,8	0,9	1,1	1,2
0,4	0,05	5,7	9,4	13,4	17,7	22,4	27,1	32,1	37,0	42,3	47,6	53,0
	10	2,3	4,0	5,7	7,4	9,4	11,4	13,4	15,6	17,7	20,0	22,4
	15	1,4	2,3	3,4	4,5	5,6	6,8	8,1	9,4	10,6	12,0	13,4
	20	0,9	1,6	2,3	3,1	4,0	4,8	5,7	6,6	7,4	8,4	9,4
	25	0,8	1,3	1,8	2,3	2,9	3,6	4,3	4,9	5,6	6,3	7,1
	30	0,6	1,0	1,4	1,8	2,3	2,9	3,4	4,0	4,5	5,1	5,7
	40		0,7	1,0	1,3	1,7	2,0	2,3	2,7	3,1	3,5	4,0
	50		0,5	0,7	0,9	1,2	1,5	1,8	2,1	2,3	2,6	2,9
	60			0,6	0,8	1,0	1,2	1,4	1,6	1,8	2,1	2,3
0,5	0,05	13,6	23,5	34,4	46,5	59,2	72,7	87,0	101,7	117,0	132,8	149,2
	10	5,4	9,4	13,8	18,6	23,6	29,0	34,8	40,6	46,8	53,2	59,7
	15	3,2	5,4	7,9	10,8	13,6	16,8	20,2	23,5	27,0	30,6	34,4
	20	2,2	3,7	5,4	7,3	9,4	11,6	13,8	16,2	18,6	21,1	23,6
	25	1,6	2,8	4,0	5,5	7,0	8,6	10,2	11,9	13,6	15,6	17,5
	30	1,3	2,2	3,2	4,3	5,4	6,7	8,1	9,4	10,8	12,2	13,8
	40	0,8	1,4	2,1	2,9	3,7	4,6	5,4	6,3	7,3	8,4	9,4
	50	0,6	1,1	1,6	2,2	2,7	3,3	4,0	4,8	5,5	6,2	7,0
	60	0,5	0,8	1,2	1,7	2,2	2,7	3,2	3,7	4,3	4,9	5,4
0,6	0,05	37,6	67,0	101,1	139,0	180,3	224,8	272,1	322,0	374,1	428,8	485,6
	10	13,9	24,9	37,3	51,4	68,3	84,7	100,4	118,8	138,2	158,2	179,2
	15	7,9	13,9	21,0	28,9	37,6	46,8	56,6	67,0	77,9	89,3	101,1
	20	5,1	9,2	13,9	19,0	24,8	30,9	37,3	44,1	51,4	58,7	66,6
	25	3,8	6,7	10,2	13,9	18,1	22,5	27,2	32,3	37,6	43,0	48,7
	30	3,0	5,1	7,7	10,7	13,9	17,2	20,8	24,8	28,7	33,0	37,3
	40	2,0	3,4	5,1	7,1	9,2	11,5	13,9	16,4	19,0	21,8	24,8
	50	1,3	2,5	3,8	5,1	6,7	8,4	10,0	12,0	13,9	15,9	18,1
	60	1,1	2,0	3,0	3,9	5,1	6,4	7,7	9,2	10,7	12,3	13,9

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TABELLE 3. STAUBNIEDERSCHLAG IN [g/m² d] BEI DER WINDGESCHWINDIGKEIT $v=2$ [m/sec] FÜR EINEN AUSWURF VON $Q=100$ [g/sec]

		Höhe [m]										
n	C_z [cm$^{n/2}$]	20	30	40	50	60	70	80	90	100	110	120
0,1	0,05		0,88	0,61	0,42	0,31	0,23	0,18	0,15	0,12	0,10	0,08
	10				1,21	0,95	0,75	0,61	0,51	0,43	0,36	0,31
	15						1,41	1,15	0,95	0,81	0,70	0,61
	20								1,82	1,28	1,02	0,95
	25										1,39	1,30
	30											
	40											
	50											
	60											
0,2	0,05	1,31	0,67	0,41	0,27	0,19	0,14	0,11	0,08	0,07	0,06	0,05
	10		1,82	1,30	0,92	0,68	0,51	0,40	0,33	0,27	0,22	0,19
	15			2,30	1,72	1,31	1,03	0,83	0,68	0,58	0,48	0,41
	20				2,74	2,23	1,72	1,43	1,15	0,96	0,82	0,70
	25					2,87	2,33	1,85	1,52	1,30	1,13	0 98
	30						3,34	2,79	2,35	2,01	1,77	1,57
	40									3,23	2,88	2,55
	50											
	60											
0,3	0,05	0,90	0,42	0,24	0,16	0,11	0,08	0,06	0,05	0,04	0,03	0,03
	10	2,80	1,44	0,89	0,60	0,42	0,31	0,24	0,19	0,15	0,12	0,10
	15		2,73	1,69	1,20	0,90	0,68	0,52	0,42	0,34	0,28	0,24
	20		4,33	2,67	1,92	1,47	1,16	0,93	0,76	0,63	0,53	0,46
	25			3,94	2,86	2,12	1,64	1,30	1,07	0,93	0,75	0,67
	30				4,72	3,54	2,63	2,17	1,85	1,57	1,33	1,13
	40					5,35	4,08	3,39	3,13	2,52	1,98	1,87
	50						5,99	4,76	4,12	3,57	3,13	2,72
	60								5,73	4,72	4,08	3,57
0,4	0,05	0,53	0,24	0,13	0,08	0,06	0,04	0,03	0,03	0,02	0,02	0,01
	10	1,95	0,87	0,52	0,34	0,23	0,17	0,13	0,10	0,09	0,07	0,06
	15	3,85	1,82	1,10	0,74	0,53	0,40	0,30	0,24	0,19	0,16	0,13
	20	5,55	2,90	1,77	1,22	0,88	0,65	0,50	0,40	0,33	0,27	0,23
	25	8,13	4,21	2,88	1,96	1,41	1,05	0,81	0,65	0,53	0,44	0,38
	30		5,80	4,48	3,17	2,38	1,87	1,49	1,19	0,99	0,84	0,73
	40			6,06	4,55	3,43	2,74	2,23	1,85	1,54	1,30	1,11
	50				6,58	5,52	4,49	3,70	3,08	2,60	2,22	1,94
	60				8,74	7,00	5,59	4,51	3,72	3,17	2,78	2,35
0,5	0,05	0,29	0,13	0,07	0,05	0,03	0,02	0,02	0,01	0,01	0,01	0,01
	10	1,14	0,48	0,28	0,18	0,13	0,10	0,08	0,06	0,05	0,04	0,03
	15	2,48	1,09	0,63	0,42	0,30	0,22	0,17	0,13	0,11	0,09	0,07
	20	4,26	1,94	1,14	0,74	0,52	0,38	0,29	0,23	0,19	0,16	0,13
	25	6,15	3,08	1,79	1,16	0,81	0,60	0,46	0,36	0,29	0,24	0,20
	30	8,00	4,12	2,52	1,65	1,14	0,84	0,66	0,52	0,42	0,35	0,29
	40	12,42	6,82	4,26	2,86	2,04	1,52	1,16	0,92	0,75	0,62	0,52
	50		10,13	6,12	4,21	3,05	2,27	1,79	1,41	1,15	0,96	0,81
	60		14,47	8,00	5,88	4,26	3,23	2,52	2,02	1,64	1,36	1,14
0,6	0,05	0,16	0,07	0,04	0,03	0,02	0,01	0,01	0,01	0,01	0,01	0,00
	10	0,66	0,29	0,16	0,10	0,07	0,05	0,04	0,03	0,03	0,02	0,02
	15	1,46	0,59	0,35	0,23	0,16	0,12	0,09	0,07	0,06	0,05	0,04
	20	2,60	1,06	0,62	0,38	0,26	0,18	0,13	0,11	0,09	0,08	0,07
	25	3,94	1,79	1,02	0,65	0,45	0,33	0,26	0,20	0,16	0,13	0,11
	30	5,56	2,44	1,46	0,94	0,66	0,49	0,37	0,29	0,24	0,20	0,16
	40	9.30	4,12	2,45	1,60	1,08	0,75	0,56	0,44	0,36	0,29	0,24
	50	13,16	6,45	3,96	2,61	1,82	1,34	1,04	0,81	0,66	0,54	0,47
	60	17,54	9,35	5,68	3,70	2,47	1,79	1,33	1,05	0,85	0,67	0,56

TABELLE 4. STAUBNIEDERSCHLAG IN [g/m² d] BEI DER WINDGESCHWINDIGKEIT $v = 4$ [m/sec] FÜR EINEN AUSWURF VON $Q = 100$ [g/sec]

		Höhe [m]										
n	C_z[cm$^{n/2}$]	20	30	40	50	60	70	80	90	100	110	120
0,1	0,05		1,64	1,14	0,78	0,58	0,43	0,34	0,28	0,22	0,19	0,15
	10				2,26	1,77	1,40	1,14	0,95	0,80	0,67	0,58
	15						2,63	2,15	1,77	1,51	1,31	1,14
	20								3,40	2,39	1,90	1,77
	25										2,59	2,43
	30											
	40											
	50											
	60											
0,2	0,05	2,28	1,17	0,71	0,47	0,33	0,24	0,19	0,14	0,12	0,10	0,09
	10		3,17	2,26	1,60	1,80	0,89	0,70	0,57	0,47	0,38	0,33
	15			4,00	2,99	2,28	1,79	1,44	1,18	1,01	0,84	0,71
	20				4,77	3,88	2,99	2,49	2,00	1,67	1,43	1,22
	25					4,99	4,05	3,22	2,64	2,09	1,97	1,71
	30						5,81	4,85	4,09	3,50	3,08	2,73
	40									5,62	5,01	4,44
	50											
	60											
0,3	0,05	1,46	0,68	0,39	0,26	0,18	0,13	0,10	0,08	0,07	0,05	0,05
	10	4,55	2,34	1,45	0,98	0,68	0,50	0,39	0,31	0,24	0,20	0,16
	15		4,44	2,75	1,95	1,46	1,11	0,85	0,68	0,55	0,46	0,39
	20		7,04	4,34	3,12	2,39	1,89	1,51	1,24	1,02	0,86	0,75
	25			6,40	4,65	3,45	2,67	2,11	1,74	1,51	1,22	1,09
	30				7,67	5,75	4,27	3,53	3,01	2,55	2,16	1,84
	40					8,69	6,63	5,51	5,09	4,10	3,22	3,04
	50						9,73	7,74	6,70	5,80	5,09	4,42
	60								9,31	7,67	6,63	5,80
0,4	0,05	0,80	0,36	0,20	0,12	0,09	0,06	0,05	0,04	0,03	0,02	0,02
	10	2,96	1,32	0,79	0,52	0,35	0,26	0,20	0,15	0,14	0,11	0,09
	15	5,84	2,76	1,67	1,12	0,80	0,61	0,45	0,36	0,29	0,24	0,20
	20	8,41	4,40	2,68	1,85	1,33	0,99	0,76	0,61	0,50	0,41	0,35
	25	12,33	6,38	4,37	2,97	2,14	1,59	1,23	0,99	0,80	0,67	0,58
	30		8,79	6,79	4,81	3,61	2,83	2,26	1,80	1,50	1,27	1,11
	40			9,19	6,90	5,20	4,15	3,38	2,80	2,33	1,97	1,68
	50				9,98	8,37	6,81	5,61	4,67	3,94	3,37	2,94
	60				13,25	10,61	8,47	6,84	5,64	4,81	4,21	3,56
0,5	0,05	0,41	0,18	0,10	0,07	0,04	0,03	0,02	0,01	0,01	0,01	0,01
	10	1,61	0,68	0,40	0,25	0,18	0,14	0,11	0,08	0,07	0,06	0,04
	15	3,51	1,54	0,89	0,59	0,42	0,31	0,24	0,18	0,16	0,13	0,10
	20	6,02	2,74	1,61	1,05	0,74	0,54	0,41	0,33	0,27	0,23	0,18
	25	8,70	4,36	2,53	1,64	1,15	0,85	0,65	0,51	0,41	0,34	0,28
	30	11,31	5,83	3,56	2,33	1,61	1,19	0,93	0,74	0,59	0,49	0,41
	40	17,56	9,64	6,02	4,04	2,88	2,15	1,64	1,30	1,06	0,88	0,74
	50		14,32	8,65	5,95	4,31	3,21	2,53	1,99	1,63	1,36	1,15
	60		20,46	11,31	8,31	6,02	4,57	3,56	2,86	2,32	1,92	1,62
0,6	0,05	0,21	0,09	0,05	0,04	0,03	0,02	0,02	0,01	0,01	0,01	0,01
	10	0,87	0,38	0,21	0,13	0,09	0,07	0,05	0,04	0,04	0,03	0,03
	15	1,93	0,78	0,46	0,30	0,21	0,16	0,12	0,09	0,08	0,07	0,05
	20	3,43	1,40	0,82	0,50	0,34	0,24	0,17	0,15	0,12	0,11	0,09
	25	5,20	2,36	1,35	0,86	0,59	0,44	0,34	0,26	0,21	0,17	0,15
	30	7,34	3,22	1,93	1,24	0,87	0,65	0,49	0,38	0,32	0,26	0,21
	40	12,28	5,44	3,23	2,11	1,43	0,99	0,74	0,58	0,48	0,38	0,32
	50	17,37	8,51	5,23	3,45	2,40	1,77	1,37	1,07	0,87	0,71	0,62
	60	23,15	12,34	7,50	4,88	3,26	2,36	1,76	1,39	1,12	0,88	0,74

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TABELLE 5. STAUBNIEDERSCHLAG IN [g/m² d] BEI DER WINDGESCHWINDIGKEIT $v=6$ [m/sec] FÜR EINEN AUSWURF VON $Q=100$ [g/sec]

		Höhe [m]										
n	C_z[cm$^{n/z}$]	20	30	40	50	60	70	80	90	100	110	120
0,1	0,05		2,37	1,64	1,13	0,83	0,62	0,48	0,40	0,32	0,27	0,22
	10				3,25	2,55	2,02	1,64	1,37	1,16	0,97	0,83
	15						3,79	3,09	2,55	2,18	1,88	1,64
	20								4,89	3,44	2,74	2,55
	25										3,74	3,49
	30											
	40											
	50											
	60											
0,2	0,05	3,15	1,61	0,99	0,65	0,46	0,34	0,26	0,19	0,17	0,14	0,12
	10		4,38	3,13	2,22	1,64	1,23	0,96	0,79	0,65	0,53	0,46
	15			5,54	4,14	3,15	2,48	2,00	1,64	1,40	1,16	0,99
	20				6,60	5,37	4,14	3,44	2,77	2,31	1,97	1,69
	25					6,91	5,61	4,45	3,66	3,13	2,72	2,36
	30						8,04	6,72	5,66	4,84	4,26	3,78
	40									7,78	6,94	6,14
	50											
	60											
0,3	0,05	1,94	0,91	0,52	0,35	0,24	0,17	0,13	0,11	0,09	0,06	0,06
	10	6,04	3,11	1,92	1,29	0,91	0,67	0,52	0,41	0,32	0,26	0,22
	15		5,89	3,65	2,59	1,94	1,47	1,12	0,91	0,73	0,60	0,52
	20		9,34	5,76	4,14	3,17	2,50	2,01	1,64	1,36	1,14	0,99
	25			8,50	6,17	4,57	3,54	2,81	2,31	2,01	1,62	1,45
	30				10,19	7,64	5,68	4,68	3,99	3,39	2,87	2,44
	40					11,55	8,80	7,32	6,75	5,44	4,27	4,04
	50						12,93	10,27	8,89	7,70	6,75	5,87
	60								12,37	10,19	8,80	7,70
0,4	0,05	1,02	0,46	0,25	0,15	0,12	0,08	0,06	0,06	0,04	0,04	0,02
	10	3,77	1,68	1,01	0,66	0,44	0,33	0,25	0,19	0,17	0,14	0,12
	15	7,44	3,52	2,13	1,43	1,02	0,77	0,58	0,46	0,37	0,31	0,25
	20	10,73	5,61	3,42	2,36	1,70	1,26	0,97	0,77	0,64	0,52	0,44
	25	15,72	8,14	5,57	3,79	2,73	2,03	1,57	1,26	1,02	0,85	0,73
	30		11,21	8,66	6,13	4,60	3,61	2,88	2,30	1,91	1,62	1,41
	40			11,71	8,80	6,63	5,30	4,81	3,58	2,98	2,51	2,15
	50				12,72	10,67	8,68	7,15	5,95	5,03	4,29	3,75
	60				16,89	13,53	10,81	8,72	7,19	6,13	5,37	4,54
0,5	0,05	0,50	0,23	0,12	0,09	0,05	0,03	0,03	0,02	0,02	0,02	0,02
	10	1,97	0,83	0,48	0,31	0,23	0,17	0,14	0,10	0,09	0,07	0,05
	15	4,30	1,89	1,09	0,73	0,52	0,38	0,29	0,23	0,19	0,16	0,12
	20	7,38	3,36	1,97	1,28	0,90	0,66	0,50	0,40	0,33	0,28	0,23
	25	10,65	5,33	3,10	2,01	1,40	1,04	0,80	0,62	0,50	0,42	0,35
	30	13,86	7,14	4,36	2,86	1,97	1,45	1,14	0,90	0,73	0,61	0,50
	40	21,51	11,81	7,38	4,95	3,53	2,63	2,01	1,59	1,30	1,07	0,90
	50		17,55	10,60	7,29	5,28	3,93	3,10	2,44	1,99	1,66	1,40
	60		25,06	13,86	10,18	7,38	5,59	4,36	3,50	2,84	2,36	1,97
0,6	0,05	0,25	0,11	0,06	0,05	0,03	0,02	0,02	0,02	0,02	0,02	0,02
	10	1,02	0,45	0,25	0,16	0,11	0,08	0,06	0,05	0,05	0,03	0,03
	15	2,27	0,92	0,54	0,36	0,25	0,19	0,14	0,11	0,09	0,08	0,06
	20	4,04	1,65	0,96	0,59	0,40	0,28	0,20	0,17	0,14	0,12	0,11
	25	6,11	2,78	1,58	1,01	0,70	0,51	0,40	0,31	0,25	0,20	0,17
	30	8,63	3,79	2,27	1,46	1,02	0,76	0,57	0,45	0,37	0,31	0,25
	40	14,43	6,39	3,80	2,48	1,68	1,16	0,87	0,68	0,56	0,45	0,37
	50	20,42	10,01	6,15	4,05	2,82	2,08	1,61	1,26	1,02	0,84	0,73
	60	27,22	14,51	8,82	5,74	3,83	2,78	2,06	1,63	1,32	1,04	0,87

TABELLE 6. STAUBNIEDERSCHLAG IN [g/m² d] BEI DER WINDGESCHWINDIGKEIT $v=8$ [m/sec] FÜR EINEN AUSWURF VON $Q=100$ [g/sec]

		Höhe [m]										
n	C_z[cm$^{n/2}$]	20	30	40	50	60	70	80	90	100	110	120
0,1	0,05		3,06	2,12	1,46	1,08	0,80	0,63	0,52	0,42	0,35	0,28
	10				4,21	3,31	2,61	2,12	1,78	1,50	1,25	1,08
	15						4,91	4,00	3,31	2,82	2,44	2,12
	20								6,34	4,46	3,55	3,31
	25										4,84	4,53
	30											
	40											
	50											
	60											
0,2	0,05	3,97	2,03	1,24	0,82	0,58	0,42	0,33	0,24	0,21	0,18	0,15
	10		5,52	3,94	2,79	2,06	1,55	1,21	1,00	0,82	0,67	0,58
	15			6,97	5,21	3,97	3,12	2,52	2,06	1,76	1,45	1,24
	20				8,30	6,76	5,21	4,33	3,49	2,91	2,49	2,12
	25					8,70	7,06	5,61	4,61	3,94	3,43	2,97
	30						10,12	8,46	7,12	6,09	5,36	4,76
	40									9,79	8,73	7,73
	50											
	60											
0,3	0,05	2,38	1,11	0,63	0,42	0,29	0,21	0,16	0,13	0,11	0,08	0,08
	10	7,39	3,80	2,35	1,58	1,11	0,82	0,63	0,50	0,40	0,32	0,26
	15		7,20	4,46	3,17	2,38	1,79	1,37	1,11	0,90	0,74	0,63
	20		11,43	7,05	5,07	3,88	3,06	2,45	2,01	1,66	1,40	1,21
	25			10,40	7,55	5,59	4,33	3,43	2,82	2,45	1,98	1,77
	30				12,46	9,34	6,94	5,73	4,88	4,14	3,51	2,98
	40					14,12	10,77	8,95	8,26	6,65	5,23	4,93
	50						15,81	12,56	10,87	9,42	8,26	7,18
	60								15,12	12,46	10,77	9,42
0,4	0,05	1,22	0,55	0,30	0,18	0,14	0,09	0,07	0,07	0,05	0,05	0,02
	10	4,48	2,00	1,19	0,78	0,53	0,39	0,30	0,23	0,21	0,16	0,14
	15	8,84	4,18	2,53	1,70	1,22	0,92	0,69	0,55	0,44	0,37	0,30
	20	12,75	6,66	4,07	2,80	2,02	1,49	1,15	0,92	0,76	0,62	0,53
	25	18,67	9,67	6,62	4,50	3,24	2,41	1,86	1,49	1,22	1,01	0,87
	30		13,32	10,29	7,28	5,47	4,30	3,42	2,73	2,27	1,93	1,68
	40			13,92	10,45	7,88	6,29	5,12	4,25	3,54	2,99	2,55
	50				15,11	12,68	10,31	8,50	7,07	5,97	5,10	4,46
	60				20,08	16,08	12,84	10,36	8,54	7,28	6,39	5,40
0,5	0,05	0,58	0,16	0,14	0,10	0,06	0,04	0,04	0,02	0,02	0,02	0,02
	10	2,28	0,96	0,56	0,36	0,26	0,20	0,16	0,12	0,10	0,08	0,06
	15	4,96	2,18	1,26	0,84	0,60	0,44	0,34	0,26	0,22	0,18	0,14
	20	8,52	3,88	2,28	1,48	1,04	0,76	0,58	0,46	0,38	0,32	0,26
	25	12,30	6,16	3,58	2,32	1,62	1,20	0,92	0,72	0,58	0,48	0,40
	30	16,00	8,24	5,04	3,30	2,28	1,68	1,32	1,04	0,82	0,70	0,58
	40	24,84	13,64	8,52	5,72	4,08	3,04	2,32	1,84	1,50	1,24	1,04
	50		20,26	12,24	8,42	6,10	4,54	3,58	2,82	2,30	1,92	1,62
	60		28,94	16,00	11,76	8,52	6,46	5,04	4,04	3,28	2,72	2,28
0,6	0,05	0,28	0,12	0,07	0,05	0,03	0,02	0,02	0,02	0,02	0,02	0,00
	10	1,15	0,50	0,28	0,17	0,12	0,09	0,07	0,05	0,05	0,03	0,03
	15	2,54	1,03	0,61	0,40	0,28	0,21	0,16	0,12	0,10	0,09	0,07
	20	4,53	1,85	1,08	0,66	0,45	0,31	0,23	0,19	0,16	0,14	0,12
	25	6,86	3,12	1,78	1,13	0,78	0,57	0,45	0,35	0,28	0,23	0,19
	30	9,68	4,25	2,54	1,64	1,15	0,85	0,64	0,50	0,42	0,35	0,28
	40	16,19	7,17	4,27	2,79	1,88	1,31	0,97	0,77	0,63	0,50	0,42
	50	22,89	11,23	6,89	4,54	3,17	2,33	1,81	1,41	1,15	0,94	0,82
	60	30,54	16,28	9,89	6,44	4,30	3,12	2,32	1,83	1,48	1,17	0,97

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TABELLE 7. ENTFERNUNG DES MAXIMALEN STAUBNIEDERSCHLAGES (IN km)

		Höhe [m]										
n	C_z[cm$^{n/z}$]	20	30	40	50	60	70	80	90	100	110	120
0,1	0,05		0,8	1,0	1,3	1,5	1,8	2,1	2,4	2,6	2,9	3,2
	10				0,6	0,7	0,9	1,0	1,1	1,3	1,4	1,5
	15						0,6	0,7	0,7	0,8	0,9	1,0
	20								0,6	0,6	0,7	0,7
	25										0,6	0,6
	30											
	40											
	50											
	60											
0,2	0,05	0,9	1,4	1,9	2,4	3,0	3,6	4,1	4,7	5,3	5,9	6,5
	10		0,6	0,9	1,1	1,4	1,6	1,9	2,2	2,5	2,7	3,0
	15			0,6	0,7	0,9	1,0	1,2	1,4	1,6	1,7	1,9
	20				0,5	0,6	0,8	0,9	1,0	1,2	1,3	1,4
	25					0,5	0,6	0,7	0,8	0,9	1,0	1,1
	30						0,5	0,6	0,6	0,7	0,8	0,9
	40									0,5	0,6	0,6
	50											
	60											
0,3	0,05	1,7	2,8	3,9	5,1	6,3	7,5	8,8	10,1	11,5	12,8	14,2
	10	0,8	1,2	1,7	2,2	2,8	3,3	3,9	4,5	5,0	5,7	6,2
	15		0,7	1,1	1,4	1,7	2,1	2,4	2,8	3,1	3,5	3,9
	20		0,5	0,8	1,0	1,2	1,5	1,7	2,0	2,2	2,5	2,8
	25			0,6	0,8	0,9	1,1	1,3	1,5	1,7	1,9	2,1
	30				0,6	0,8	0,9	1,1	1,2	1,4	1,6	1,7
	40					0,5	0,7	0,8	0,9	1,0	1,1	1,2
	50						0,5	0,6	0,7	0,8	0,9	0,9
	60								0,5	0,6	0,7	0,8
0,4	0,05	3,7	6,1	8,7	11,5	14,5	17,6	20,8	24,0	27,4	30,9	34,4
	10	1,5	2,6	3,7	4,8	6,1	7,4	8,7	10,1	11,5	13,0	14,5
	15	0,9	1,5	2,2	2,9	3,7	4,4	5,3	6,1	6,9	7,8	8,7
	20	0,6	1,1	1,5	2,0	2,6	3,1	3,7	4,3	4,8	5,5	6,1
	25	0,5	0,8	1,2	1,5	1,9	2,3	2,8	3,2	3,7	4,1	4,6
	30		0,6	0,9	1,2	1,5	1,9	2,2	2,6	2,9	3,3	3,7
	40			0,6	0,9	1,1	1,3	1,5	1,8	2,0	2,3	2,6
	50				0,6	0,8	1,0	1,2	1,4	1,5	1,7	1,9
	60				0,5	0,6	0,8	0,9	1,1	1,2	1,4	1,5
0,5	0,05	8,6	14,8	21,7	29,3	37,3	45,8	54,8	64,1	73,7	83,7	94,0
	10	3,4	5,9	8,7	11,7	14,9	18,3	21,9	25,6	29,5	33,5	37,6
	15	2,0	3,4	5,0	6,8	8,6	10,6	12,7	14,8	17,0	19,3	21,7
	20	1,4	2,3	3,4	4,6	5,9	7,3	8,7	10,2	11,7	13,3	14,9
	25	1,0	1,7	2,5	3,4	4,4	5,4	6,4	7,5	8,6	9,8	11,0
	30	0,8	1,4	2,0	2,7	3,4	4,2	5,1	5,9	6,8	7,7	8,7
	40	0,5	0,9	1,4	1,8	2,3	2,9	3,4	4,0	4,6	5,3	5,9
	50		0,7	1,0	1,4	1,7	2,1	2,6	3,0	3,4	3,9	4,4
	60		0,5	0,8	1,1	1,4	1,7	2,0	2,3	2,7	3,1	3,4
0,6	0,05	22,9	40,8	61,6	84,7	109,9	137,0	165,8	196,2	228,0	261,3	295,9
	10	8,5	15,2	22,7	31,3	40,6	50,6	61,2	72,4	84,2	96,4	109,2
	15	4,8	8,5	12,8	17,6	22,9	28,5	34,5	40,8	47,5	54,5	61,6
	20	3,1	5,6	8,5	11,6	15,1	18,8	22,7	26,9	31,3	35,8	40,6
	25	2,3	4,1	6,2	8,5	11,0	13,7	16,6	19,7	22,9	26,2	29,7
	30	1,8	3,1	4,7	6,5	8,5	10,5	12,7	15,1	17,5	20,1	22,7
	40	1,2	2,1	3,1	4,3	5,6	7,0	8,5	10,0	11,6	13,3	15,1
	50	0,8	1,5	2,3	3,1	4,1	5,1	6,1	7,3	8,5	9,7	11,0
	60	0,7	1,2	1,8	2,4	3,1	3,9	4,7	5,6	6,5	7,5	8,5

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Int. J. Air Poll. Pergamon Press 1959. Vol. 2, pp. 42–50. Printed in Great Britain

SMOKE PLUMES AS QUANTITATIVE AIR POLLUTION INDICES

FRANK GIFFORD, Jr.
Weather Bureau Office, Oak Ridge, Tennessee
(*Received* 1 *April* 1959)

Abstract—By combining the familiar Gaussian distribution for atmospheric dispersion from a continuous source, written in a general form, with ROBERTS' opacity theory for the edge of a smoke plume, and then introducing particular dispersion models (e.g. SUTTON's and FRENKIEL's), it is possible to obtain very simple formulae for dispersion coefficients. These can be expressed as ratios of gross measurements of the visible plume, namely the total plume length, x_t, the maximum width, $2Y_m$, and the distance from the source of this maximum width, x_m.

The principal results are the following formulae:

$$\overline{v^2} = U^2 e(Y_m/x_T)^2; \qquad \overline{w^2} = U^2 e(Z_m/x_T)^2$$
$$C_y^2 = 2x_T^n e(Y_m/x_T)^2; \qquad C_z = 2x_T^n e(Z_m/x_T)^2$$
$$\overline{v^2} = U^2(Y_m/x_m)^2; \qquad \overline{w^2} = U^2(Z_m/x_m)^2$$
$$C_y^2 = 2x_m^n(Y_m/x_m)^2; \qquad C_z^2 = 2x_m^n(Z_m/x_m)^2.$$

In these, C_y and C_z are the so-called " virtual diffusion coefficients ", and n the stability parameter, of SUTTON's diffusion theory; and $\overline{v^2}$ and $\overline{w^2}$ are the Lagrangian turbulence intensities as employed, for example, in FRENKIEL's diffusion studies.

The required plume measurements are readily obtained visually or from photographs, since only ratios of plume dimensions are required, not absolute magnitudes. Some form of time averaging of the plume observations is desirable, however. This could be accomplished by taking long time-exposure photographs, or by other methods. The results seem likely to be of particular use in air pollution field studies, in that a rapid, direct estimate of the atmosphere's dispersive power can be made from simple smoke plume measurements.

1. INTRODUCTION

STUDY of smoke puffs and plumes as indices of atmospheric dispersion has always been widespread probably because it is a simple, direct approach to the air pollution problem. Smoke has been used both as a qualitative and a quantitative atmospheric dispersion index with some success. Quantitative methods stem from ROBERTS' (1923) " opacity theory ", which has been used by SUTTON (1932), and later by nearly all modern workers (FRENKIEL, 1956; KELLOGG, 1956; HOLLAND, 1953; MOSES, 1956, etc.). The idea of this method is that smoke particles act to obscure the background, and when enough of them are along a line of sight the background disappears. This is the " edge " of the smoke. Often, a second assumption has been combined with the opacity idea, namely that the visible plume edge represents a certain percentage of some reference concentration. Another assumption that has invariably been introduced is that the puff or plume is described by a certain theoretical model of dispersion. Neither of these assumptions is necessary, as was indicated in a recent study of smoke puffs (GIFFORD, 1957). However, several simple, potentially useful formulae relating diffusion coefficients to easily measured puff or plume properties follow, once some particular dispersion model is assumed. The purpose of this

study is to present some of these relationships in the hope that others working with smoke plumes may find them of some interest.

2. THE OPACITY METHOD

The steady state concentration from a continuously emitting point source at the origin of x-, y-, z-axes is usually expressed mathematically by a relationship of the following type:

$$X_{(x,y,z)} = \frac{Q}{2\pi[\overline{Y^2}(x/U)\overline{Z^2}(x/U)]^{\frac{1}{2}}U} \cdot \exp-[y^2/2\overline{Y^2}(x/U)]\exp-[z^2/2\overline{Z^2}(x/U)]; \quad (1)$$

X is the concentration of material at point (x, y, z) emitted by a source of strength Q units per second, located at $(0, 0, 0)$; U is the mean wind speed, and $x = Ut$. The notation is fairly standard (see U.S. WEATHER BUREAU (1955) for an extensive review). The horizontal and vertical variances, $\overline{Y^2}(t)$, and $\overline{Z^2}(t)$, of the plume concentration distribution depend on the dispersion time t in some not yet specified way.

The question of the applicability of a Gaussian relationship such as equation (1) to dispersion problems in the atmosphere is moot at present. Although the dispersion models most widely used in practical applications, i.e. those of SUTTON (1932), FRENKIEL (1956) and ROBERTS (1923), are all special cases of (1), yet it should be realized that the Gaussian model of dispersion is a plausible assumption, rather than a proved theoretical fact [cf. the discussion by BATCHELOR (1952), pp. 360–1]. Recent experimental dispersion studies by HAY and PASQUILL (1957), and BARAD and HAUGEN (1959), lend a certain amount of support to (but by no means prove) a Gaussian model, even where the source is quite near the ground.

The effect of sampling (averaging) time on dispersion has recently been studied by STEWART *et al.* (1958) and by CRAMER (1959). The interested reader is referred to these discussions for details.

If the plume is viewed from a fairly great vertical distance, the total density of smoke particles along a line of sight is

$$\int_{-\infty}^{\infty} X\,dz = \frac{Q\exp(-y^2/2\overline{Y^2})}{2\pi(\overline{Y^2}\overline{Z^2})^{\frac{1}{2}}U}\int_{-\infty}^{\infty}\exp(-z^2/2\overline{Z^2})\,dz. \quad (2)$$

If there is a fixed value of this integrated concentration, say X_e, corresponding to the visible edge of the plume, and if this value occurs at distance Y from the x-axis, then

$$\frac{X_e}{Q} = \frac{\exp(-Y^2/2\overline{Y^2})}{(2\pi\,\overline{Y^2})^{\frac{1}{2}}U}. \quad (3)$$

At $Y = 0$ (i.e. at the end of the plume)

$$X_e/Q = [2\pi\,\overline{Y^2}(T)U^2]^{-\frac{1}{2}} \quad (4)$$

where $\overline{Y^2}(T)$ is the (constant) value of $\overline{Y^2}$ that applies at the plume end. Equating (3) and (4), and differentiating logarithmically with respect to x/U, it can be shown that

$$\frac{d(Y^2)}{dx} = \frac{d\,\overline{Y^2}}{dx}\left(\frac{Y^2 - \overline{Y^2}}{\overline{Y^2}}\right).$$

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Now when $Y^2 = \overline{Y^2}$, $d(Y^2)/dx = 0$. This will, of course, occur at the widest dimension of the plume, say at the point where the half-width is Y_m. It then follows from (3) and (4) that the constant, $\overline{Y^2}(T)$, is

$$\overline{Y^2}(T) = eY_m^2 \tag{5}$$

where e is the base of natural logarithms. From these relationships a formula relating $Y^2(t)$ to Y is obtained in just the same way as for the case of a smoke puff (GIFFORD, 1957; KELLOGG, 1956). By equating the right-hand sides of (3) and (4), squaring, and taking logarithms, it is found that

$$\overline{Y^2}(x/U) = Y^2\left[\ln\left(\frac{eY_m^2}{\overline{Y^2}(x/U)}\right)\right]^{-1}. \tag{6}$$

From this transcendental equation, $\overline{Y^2}(x/U) = \overline{Y^2}(t)$ may be determined by means of visual or photographic observations of Y, the plume half-width. (It goes without saying that the whole idea can be adapted to vertical plume observations, by integrating, and observing, in the y-direction. The vertical plume variance, $\overline{Z^2}$, is obtained in this way.) Fig. 1 is a plot of equation (6) in a generalized form, from which numerical values of $\overline{Y^2}$ or $\overline{Z^2}$ are readily determined.

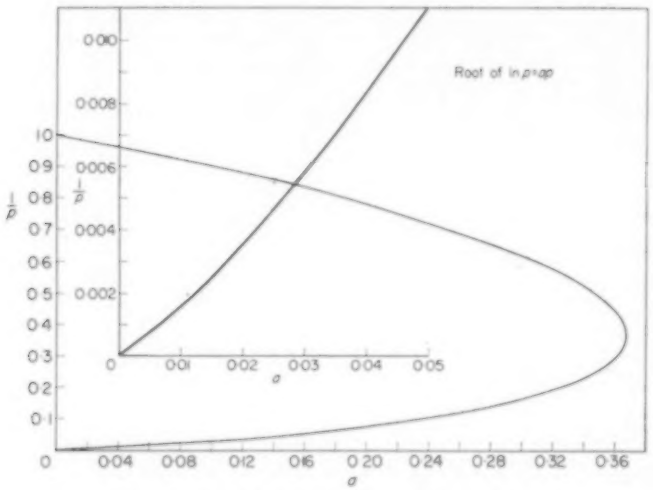

FIG. 1. Graph of roots of the equation $\ln p = ap$.

By means of the definitions

$$p = eY_m^2/\overline{Y^2}(x/U)$$

or

$$p = eZ_m^2/\overline{Z^2}(x/U),$$

and

$$a = e^{-1}(Y^2/Y_m^2),$$

or

$$a = e^{-1}(Z^2/Z_m^2)$$

equation (6) may be evaluated.

3. LIMITATIONS OF THE OPACITY METHOD

Several shortcomings of the opacity idea, such as uncertainties due to non-uniformity of background illumination, the dependence of visual contour perception

on luminosity gradients, and other intangibles, have been pointed out in past studies as well as personally to the writer. These have not been studied quantitatively and little is known about how serious they may be. In view of quantitative results such as FRENKIEL's, and BOWNE's, as well as those to be presented below, it appears that the opacity method provides at least a useful, practical tool.

A more serious restriction to the use of visually or photographically determined dimensions of plumes as dispersion indices is inherent in the nature of turbulent dispersion. At any instant, the visual or photographic appearance of a plume suggests that it is a dispersion of particles about a centerline which is itself deformed by the air turbulence. On the theoretical side, it has been recognized since the work of RICHARDSON (1926) that dispersion relative to a co-ordinate system (such as the center of a puff or plume) itself free to move with turbulent fluctuations is a distinctly different phenomenon from dispersion relative to a fixed axis, i.e. the dispersion involved in equation (1). Exhaustive treatments of the theory can be found in papers by BATCHELOR (1950, 1952). An attempt to incorporate these ideas into a rational " fluctuating plume " dispersion model was recently made by GIFFORD (1958).

The conclusion from these studies is that formulae such as equation (1), *relating dispersion to a fixed axis, can apply only to averaged conditions*, i.e. *only to the mean concentration distribution.* We should, consequently, expect the opacity theory to apply to long time-exposure photographs of plumes, such as those made with a pinhole camera by SHORR (1952). Strictly speaking, it is not correct to apply results deduced from a fixed axis dispersion model to dispersion of a single smoke puff, or to the instantaneous dispersion pattern of a single plume, relative to the plume centerline (cf. the discussion of this point by GIFFORD (1957)). Notwithstanding, such applications will be suggested in what follows; and it should be clearly understood that the only justification for this is practical expediency. Unfortunately, the above distinction has frequently been overlooked in practical diffusion studies. Where it is ignored in the following remarks, the results can have only the status of useful, practical rules-of-thumb.

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4. EXAMPLES OF USEFUL SMOKE PLUME FORMULAE

The distribution of smoke in space is completely characterized by equation (1). The only unknown quantities in equation (1) are $\overline{Y^2}$ and $\overline{Z^2}$. Practically speaking, X may also not be known. In terms of the visible plume this means we may not know X_e; but X_e may be determined, if necessary, by combining equations (4) and (5). If one assumes (as has always been done in smoke dispersion studies) some particular form for $\overline{Y^2}$, i.e. SUTTON's form

$$\overline{Y^2} = \tfrac{1}{2} C^2 X^{2-n}, \quad 0 < n < 1, \tag{7}$$

or else that employed by FRENKIEL,

$$\overline{Y^2} = \overline{v^2} t^2, \tag{8}$$

then the plume geometry is firmly fixed (so far as the mathematics is concerned). Consequently, it is reasonable that some simple geometrical measurements of the plume are all that is needed in order to determine diffusion coefficients, i.e. C or $\overline{v^2}$. Many detailed measurements of the plume geometry, or further assumptions as to visual threshold concentrations, are not necessary. In one way or another previous

smoke dispersion studies have failed to take advantage of this fact; some possibilities that have occurred to us follow.

Plume length–width ratio

Combining equation (5) with equation (8) it is found that

$$\overline{Y^2}(T) = eY_m^2 = \frac{\overline{v^2}\, x_T^2}{U^2} \tag{9}$$

where x_T is the length of the visible plume and Y_m is its half-width. From this,

$$\overline{v^2} = U^2 e \left(\frac{Y_m}{x_T}\right)^2, \tag{10}$$

i.e. we may find the diffusion parameter, $\overline{v^2}$, which is the mean square turbulence intensity, simply by determining the ratio of the plume half-width to the plume length. This is very convenient, because measurement of the ratio is quite simple compared with absolute measurement of height and length. In a similar way, the vertical turbulence intensity, $\overline{w^2}$, is given by

$$\overline{w^2} = U^2 e (Z_m/x_T)^2. \tag{10a}$$

A number of photographs (see HOLLAND (1953) for some examples) of smoke plumes generated at ground level are available at Oak Ridge, and some 25 of these were used to evaluate $\overline{w^2}$ by equation (10a). The procedure was simply to outline the plume on a photograph, and determine Z_m/x_T. The outlining process was used

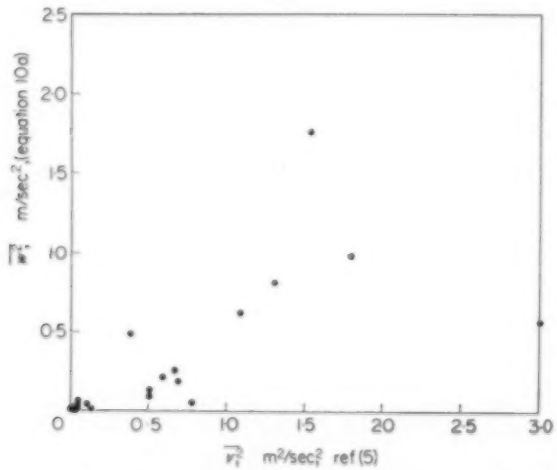

FIG. 2. Correlation of the mean square turbulence intensity $\overline{w^2}$ computed from equation (10a), with $\overline{v^2}$, from HOLLAND (1953).

to compensate (qualitatively) for the fact that the photographs are instantaneous, rather than time-averaged as required by strict application of the method, by drawing a rather smooth, generalized plume outline instead of one which followed each small wisp of smoke. The methods of combining plume photographs described by

BOWNE (1958), HILST (1957) or MOSES and CLARK (1956), are of course much preferable to this crude procedure. The resulting $\overline{w^2}$ values can be compared with $\overline{v^2}$ values determined independently from a graph of $(\overline{v^2})^{\frac{1}{2}}$ as a function of U and stability, pertaining to the same location (HOLLAND, 1953, Fig. 164).

Fig. 2 indicates the degree of relationship that was found. The coefficient of linear correlation for these data is 0·71. That $\overline{w^2}$ values determined from equation (10a) are systematically smaller than the $\overline{v^2}$ values may reflect real turbulence anisotropy near the ground. On the other hand, it may be that failure to form a proper average plume has led to an underestimate of the plume height, which would also explain the discrepancy. Perhaps it is necessary as well to recall the fact that the turbulence intensity inferred from the smoke measurements is representative of turbulent particle motions, i.e. it is a Lagrangian statistic. Its theoretical relationship to the corresponding Eulerian value, measured at a fixed point, is not yet known. Nevertheless, this result indicates that, by and large, Eulerian turbulence intensity is a good index of the plume geometry, which is to say of the concentration distribution, at least out to the distances involved (several hundred yards). The value of the correlation is not low, but might well be even higher, were direct measurements of $\overline{v^2}$ available.

If SUTTON's dispersion model, i.e. equation (7) is used, the formula corresponding to equation (10) turns out to be

$$C_y^2 = 2x_T^n e(Y_m/x_T)^2. \tag{11}$$

Thus the method can be applied to determination of SUTTON C_y values by making a rough approximation of x_T. Since x_T appears essentially as a fourth root, its precise determination is not necessary. The corresponding result for C_z is

$$C_z^2 = 2x_T^n e(Z_m/x_T)^2. \tag{11a}$$

Ratio of the maximum width-distance to the maximum width

By combining equations (3), (4) and (5), it is not difficult to prove that

$$Y_m^2 = \overline{Y^2}(x_m/U),$$

from which, with equation (8), it follows that

$$\overline{v^2} = U^2(Y_m/x_m)^2 \tag{12}$$

where x_m is the distance along the plume axis at which Y_m occurs. The corresponding relation for $\overline{w^2}$ is

$$\overline{w^2} = U^2(Z_m/x_m)^2. \tag{12a}$$

This relationship proved particularly useful in analyzing plume photographs from which the approximate maximum height, but not the end of the plume, could be determined. For some surface smoke pot photographs (59 of these now being available for these new conditions) the linear correlation coefficient of $\overline{w^2}$ determined by equation (12a) with values of $\overline{v^2}$ determined by HOLLAND's method was 0·66. For 13 elevated stack plumes, the corresponding correlation coefficient was 0·79. Again equations similar to (11) and (11a) can be derived assuming SUTTON's model, i.e. equation (7):

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$$C_y^2 = 2x_m^n(Y_m/x_m)^2; \tag{13}$$

$$C_z^2 = 2x_m^n(Z_m/x_m)^2. \tag{13a}$$

Formulae equivalent to equations (12) and (13), but expressed in terms of the K-theory, were used by RICHARDSON and PROCTOR (1926) in their study of diffusion over long distances.

Calculations of X_e

SHERWOOD (1949) gave the integrated, line-of-sight concentration value 0·33 g/m² for screening by smoke. This, of course, will depend on the kind of smoke, the background brightness, and doubtless on other factors. By combining equation (4) with equation (5) it follows that

$$X_e/Q = [(2\pi e Z_m^2)^{\frac{1}{2}} U]^{-1}. \tag{14}$$

The universal practice in previous quantitative smoke plume studies has been to assume that X_e, or the corresponding X value, represents some percentage (usually 10) of a known concentration value. HOLLAND (1953), for example, assumed the visible edge would be determined by a line-of-sight, integrated concentration equal to 10 per cent of SHERWOOD's screening figure, i.e. by the value 0·033 g/m². For the smoke sources used by HOLLAND, Q equalled 5 g/sec. Representative values of $Z_m = 20$ m, and $U = 4$ m/sec, indicate that $X_e = 0{\cdot}015$ g/m². If, as is customary, a factor of 2 to account for ground reflection is taken into consideration, agreement with HOLLAND's assumption is very close.

5. OPACITY METHOD APPLIED TO A FLUCTUATING PLUME MODEL

In an attempt to deal with the instantaneous vs. averaged aspect of smoke plumes, mentioned in Section 3 above, the writer proposed a " fluctuating plume dispersion model ". In this model, the instantaneous distribution of smoke concentration is given by the equation

$$X/Q = [2\pi U(\overline{Y^2}\,\overline{Z^2})^{\frac{1}{2}}]^{-1} \exp[-(y - D_y)^2/2\overline{Y^2}] \exp[-(z - D_z)^2/2\overline{Z^2}]. \tag{15}$$

The new terms D_y and D_z are distances from the average plume centerline at which the instantaneous plume center may be found; and, of course, these distances vary irregularly depending on the amount of meandering of the plume.

If the plume is viewed from a sufficient lateral distance, D_y will appear to be zero. Then the integrated, line-of-sight edge-concentration is given by

$$[X_e/Q = \exp[-(Z - D_z)^2/2\overline{Z^2}]/[(2\pi\,\overline{Z^2})^{\frac{1}{2}} U] = \text{constant}. \tag{16}$$

From this it is evident that at a fixed distance x from the source

$$Z = D_z + \text{constant}, \tag{17}$$

and a similar result applies to Y. If D_z is assumed to possess a Gaussian distribution, then Z will also have this distribution. Suitable data with which to check this prediction of the fluctuating plume model (i.e. time-lapse plume photographs) should not be difficult to obtain.

6. SUMMARY AND CONCLUSION

Some rule-of-thumb formulae relating atmospheric dispersion coefficients to various simple measurements of visible smoke plumes have been devised, i.e. equations (9) through (14). These follow directly from widely used mathematical models

of dispersion, i.e. equation (1) combined with equations (7), (8) or a similar assumption, when the idea of " opacity " leading to a visual edge of the plume, i.e. equation (2), is introduced. The general formula for plume dispersion, equation (7), also results directly from equation (2). Since the results presented, except for equation (15), apply only to the mean concentration distribution, it is desirable to introduce some method of averaging plume photographs or visual observations, which are usually quasi-instantaneous in nature.

The possible usefulness of these formulae, and their essential difference from previous results along this line, lies in the fact that the necessary plume measurements do not occur directly, but only as ratios. These ratios can be determined from plume photographs, or visual plume observations, comparatively easily, in that actual distances do not need to be determined; and any convenient relative length scale may be used. Visually, for example, it would appear feasible to determine plume lengths and widths using, as a measure, numbers of fingers subtended when the hand is held at arm's length. This might provide a useful rule-of-thumb for estimating dispersion in air pollution field work. Despite this degree of simplicity, it should be emphasized that the results obtained are in principle equally, i.e. neither more nor less, precise than those of previous smoke studies. Inherent limitations, discussed in a previous section, apply to *all* opacity studies equally. Therefore, it is felt that the present results may prove to be of some use in practical air pollution studies.

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DAILY AND SEASONAL POLLUTION CYCLES IN THE DETROIT–WINDSOR AREA*

R. E. MUNN† and MORRIS KATZ‡

(*Received* 26 *April* 1959)

Abstract—Previous studies, using a network of sampling stations, have revealed the broad air pollution and climatic features of the Detroit–Windsor area. In the present paper it is therefore possible to analyze in some detail the pollution records from a single sampling station at Peter and Chappell Streets, Windsor, Ontario. A deck of approximately 15,000 hourly punched IBM cards has been used to prepare frequency tabulations of concentrations of sulphur dioxide and suspended particulates vs. various wind and lapse rate classifications. The objective has been to describe the mean daily and seasonal air pollution cycles and to offer explanations for their existence.

In Section 4 sulphur dioxide frequencies are related to wind. Highest concentrations are mainly associated with unstable air and strong west or southwest winds. A separation by time of day reveals that the high concentration peak with southwest winds is rather uniformly distributed throughout the daylight hours and is caused by a looping plume from a nearby steam generating plant. The west wind peak occurs shortly after sunrise; in Section 9 the Hewson fumigation effect is offered as the probable cause. It is concluded that sulphur dioxide observations are greatly affected by neighbouring point sources and are not a good index of urban pollution.

A similar analysis in Section 5 of suspended particulate data displays quite a different pattern. High concentrations occur mainly with light winds, associated mainly with night-time inversions or morning fumigations. It is concluded that data on suspended particulates give a much more representative index of the urban area than do the sulphur dioxide data.

In Sections 6 and 7 the daily cycles of sulphur dioxide and particulate pollution are outlined without comment. There is a well-marked early morning and a secondary evening peak in most seasons.

Section 8 describes and discusses the annual cycle of pollution. Average pollution levels are highest in winter and lowest in summer. The probable cause is an increase in emissions during the winter season. Spring is similar to fall because the higher degree day totals (and resulting higher emissions) in March–April–May balance the less favorable meteorological factors in September–October–November. Additional indirect evidence is also presented to indicate that sulphur dioxide is coming primarily from elevated sources while particulates are emitted at a generally lower level.

Section 9 extends the analysis in Sections 4 and 5. Seasonal variations in weather factors are used to explain the residual features of the pollution concentration patterns for different wind directions in different seasons. The looping plume from the steam generating plant is considered fully (see Fig. 21).

Section 10 examines the morning peak in the daily pollution cycle. The variation under lapse and inversion conditions and the earlier time of occurrence in summer are offered as evidence that the peak is caused primarily by a Hewson fumigation and not by an increase in industrial and domestic activity.

Section 11 considers the evening peak in the daily pollution cycle. The authors postulate a fumigation mechanism caused by the urban heat-island effect. It is admitted that the argument is speculative but is included to promote the publication of data on the subject from other urban areas.

* Presented at the 134th National Meeting of the American Chemical Society, 7–12 September, 1958, Chicago, Illinois.

† Meteorologist, Department of Transport, Windsor, Canada. Permission to publish has been given by the Director, Meteorological Branch, Canada.

‡ Consultant, Atmospheric Pollution Services, Department of National Health and Welfare, Ottawa, Canada.

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1. INTRODUCTION

IN an urban area, ground-level concentrations of pollution show well-marked mean daily and seasonal patterns. These have been attributed in the literature to cycles of weather or emissions, or to a combination of both. Neglecting photochemical types of pollution, there are usually evident a strong early morning peak and a secondary evening peak in concentrations, when many observations are averaged. Many writers have speculated about the cause of the morning peak, whether it is due to increased industrial and domestic activity or whether it is caused primarily by the Hewson fumigation (lapse conditions near the ground, inversion aloft during the morning break-up of the inversion). The evening peak has been noted but no satisfactory explanation has been offered.

On a seasonal basis, pollution levels are usually highest in winter, although autumn is traditionally the season noted for spells of hazy weather. It is not clear from the literature whether the higher readings are caused by an increase in fuel consumption or by weather factors.

A description of the International Joint Commission study in the Detroit–Windsor area, including details of sources and character of local emissions has been presented elsewhere by KATZ and SCHUENEMAN (1958). The data from a network of pollution stations have been discussed in relation to meteorological factors by KATZ (1952) and by BAYNTON (1956). With this background knowledge of the broad pollution patterns throughout the area, it is possible in the present paper to consider in much more detail the data from a single sampling station in order to study time cycles. Concurrent records of concentrations of sulphur dioxide and of suspended particulate matter taken at the same site reveal interesting similarities and differences.

A qualitative knowledge of the meteorological diffusion and deposition processes will be assumed. Review articles on the meteorological aspects of the subject have been published in the *Air Pollution Handbook* (MAGILL *et al.*, 1956) and in the *Compendium of Meteorology* (HEWSON, 1951).

2. SOURCES OF DATA

This paper is based on IBM 101 statistical tabulations prepared by the Climatological Division of the Canadian Department of Transport. A special deck of approximately 15,000 hourly punched cards was used, based on source documents prepared in the Windsor Air Pollution Laboratory. The elements pertinent to this particular study are lapse rate, wind and concentrations of sulphur dioxide and suspended particulate matter. Other tabulations, such as pollution levels during precipitation periods, will be reported at a later date.

Lapse rate measurements employed in this paper are for the 20 ft–300 ft atmospheric layer, as observed by means of recording resistance thermometers placed on Television Tower WJBK, Detroit. Observations of winds were obtained from the Detroit City Airport records. A description of instrumentation and a discussion of the representativeness of data have been given by MUNN (1959), together with frequency tabulations of lapse rate and wind. In view of the broad class frequency intervals that have been used, the data are believed to be broadly representative of the urban area. Because of the large roughness elements in a city, the convention adopted by MUNN (1959) will be followed in this paper; namely, the use of the isothermal rather than the dry adiabatic as an arbitrary limit for significant turbulence.

Hence, " lapse conditions " will denote all positive lapse rates of temperature ; " inversion conditions " will denote zero or negative lapse rates.

The IJC Peter and Chappell sampling station is in Canada, about 4 miles to the southwest of downtown Detroit. There is relatively open country to the southeast and south with no important sources of pollution. The J. Clarke Keith steam generating plant is in Canada about $\frac{1}{2}$ of a mile to the southwest. There is a concentration of industry 2–4 miles to the southwest in Ecorse, River Rouge, and Zug Island on the U.S. side of the Detroit River. Other sources of pollution are to be found to the northwest, north and northeast in Dearborn, Detroit, and Windsor.

Sulphur dioxide was measured with a Thomas autometer. The record provides average concentrations for approximately 30 min cycles. In preference to averaging the concentrations for the entire hour, the convention was adopted of including on the punch card the reading from the cycle that was in progress at 60 min after each hour. The period of record extends from 27 July, 1955, to 31 August, 1957. September–November 1957 tabulations were not available in time for inclusion in Figs. 1–5 and 11–15; however, the data were used as a control check, as will be outlined in a later section.

In a previous study, BAYNTON (1959) compared SO_2 concentrations at two points in Detroit, three in Windsor, one at Harrow, Ontario, about 25 miles south of Windsor, and one at La Salle, Ontario, about 6 miles southwest of Windsor. Using the most centrally located station as a reference, he found little correlation with the other sampling stations in the network. It was concluded that the concentration of SO_2 is determined principally by the effect of specific point sources. Evidently, it is unrealistic to attempt to define a concentration of this gas that will be representative of the metropolitan area. The SO_2 tabulations in this study, therefore, reflect very strongly the influence of neighbouring point sources, particularly the J. Clarke Keith steam generating plant.

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Suspended particulates were measured with an AISI automatic smoke sampler (HEMEON *et al.*, 1953). Two-hourly samples of air were filtered, the optical densities of the stains determined, and the results expressed in terms of Coh/1000 ft. A Coh value was, therefore, included only on every second punch card, the reading representing an average 2-hr value. The period of record is from 27 July, 1955 to 30 November, 1957. Unfortunately, the sampler was not operated in the summer of 1956; the total number of summer cases is, therefore, only 866 as compared with about 1270 in each of the other three seasons.

In a previous study, BAYNTON (1959) compared particulate mass concentrations at four points in Detroit, two at Windsor, and one in Harrow, Ontario, using results from high volume filtration samplers operated on a 24-hr sampling period. Significant correlation coefficients were found between measurements at the reference site and all other sampling stations, including Harrow, which was 25 miles to the south in a rural area. He concluded that the concentration of airborne particulate pollution is determined principally by the synoptic weather pattern, local point sources being of secondary importance, although still present and recognizable. In another paper, BAYNTON (1956) was able to correlate particulate loadings in the Detroit–Windsor area with a number of weather factors, but excluding wind direction. It is likely that a similar study of sulphur dioxide concentrations would have been unsuccessful. It is believed, therefore, that the Coh tabulations to be presented in the

following sections reflect the general urban trend of suspended particulates, although local sources will still have some secondary influence.

3. METHOD OF ANALYSIS

There is an uneven distribution of point sources around the sampling station. In addition, the inventory of source strengths and of variations with time is not sufficiently well known for purposes of analysis. However, ground-level concentrations have been observed with some accuracy. It would therefore seem logical to try to determine whether the observed pollution patterns can be explained by meteorological factors alone. For example, a shift in prevailing wind direction from season to season would probably produce a change in mean pollution levels aside from any other factors.

If a large residual shift in concentrations with time of day or year is still apparent after all the meteorological parameters have been considered, then, perhaps, an emission cycle may be inferred indirectly.

4. VARIATIONS OF SULPHUR DIOXIDE CONCENTRATIONS WITH WIND

Figs. 1–5 display five classes of percentage frequency distributions of SO_2 concentration by wind direction on an annual and seasonal basis. In each figure, the total area under all the histograms represents 100 per cent of the data. The shaded areas indicate the percentage frequencies under inversion conditions; for example, in Fig. 1 the total shaded areas are associated with about 35 per cent of all cases. In general, the shaded areas represent night-time occurrences.

A discussion of seasonal differences will be delayed until Section 9, in an attempt to avoid consideration of too many factors at once. However, similarities that extend through all four seasons will be examined now.

The patterns formed by the shaded histograms are, in general, quite similar to those of the total histograms. At first glance, it might appear that lapse rate is not particularly important in relating SO_2 concentrations with wind directions.

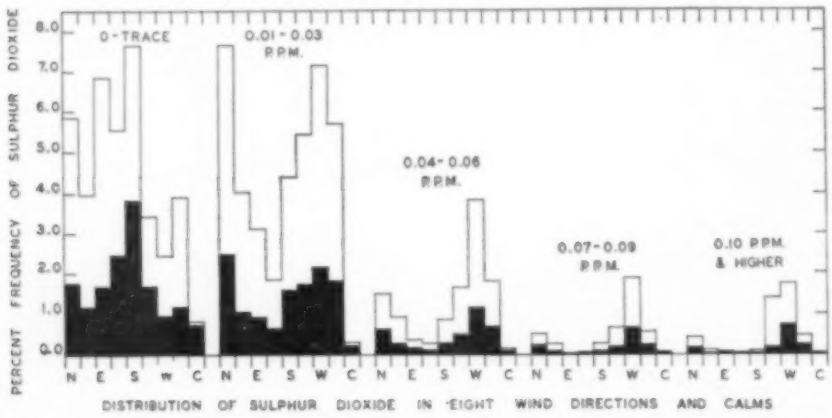
PERCENT FREQUENCY OF SULPHUR DIOXIDE
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0 - TRACE
0.01 - 0.03 P.P.M.
0.04 - 0.06 P.P.M.
0.07 - 0.09 P.P.M.
0.10 P.P.M. & HIGHER
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF SULPHUR DIOXIDE IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 1. Percentage frequency histograms of sulphur dioxide concentrations by wind direction on an annual basis. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions.

Most of the frequencies are in the range of 0 to 0·03 p.p.m. The modes in that class occur with south to east winds. This is in direct contrast to the prevailing west wind of the area and must be attributed to the location of emission sources with respect to the sampling station.

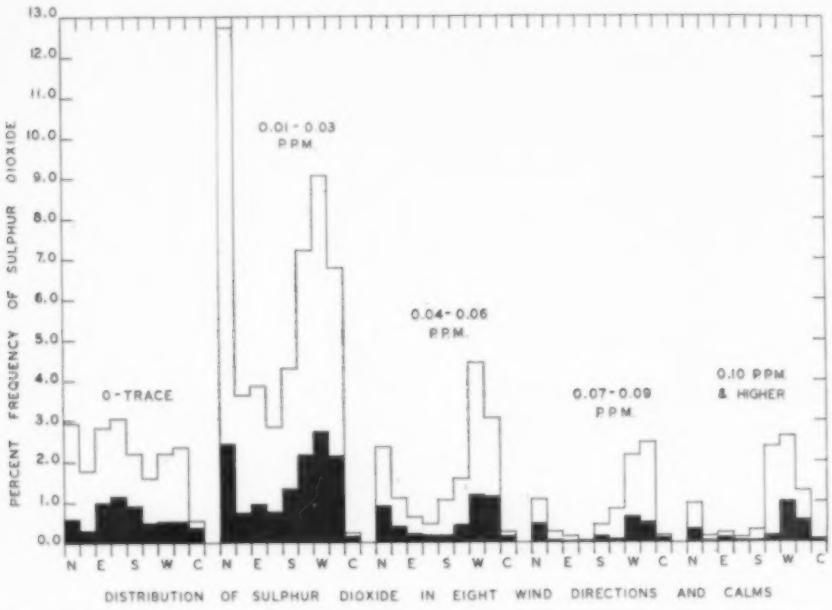

FIG. 2. Percentage frequency histograms of sulphur dioxide concentrations by wind direction for the winter months December, January and February. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions.

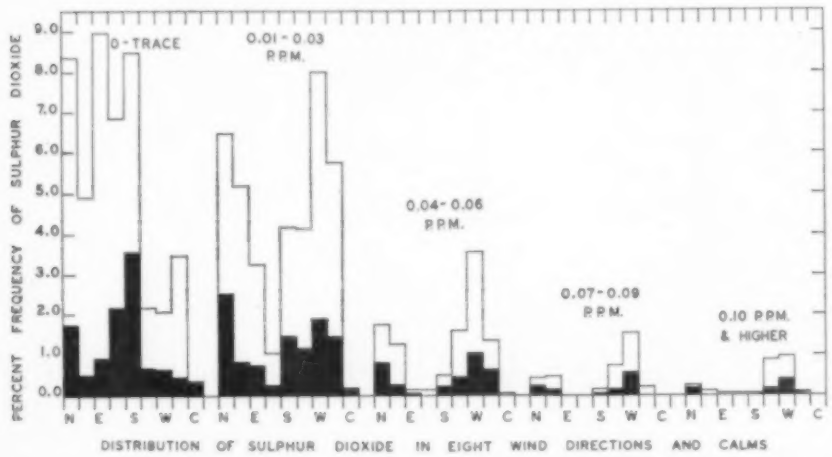

FIG. 3. Percentage frequency histograms of sulphur dioxide concentrations by wind direction for the spring months March, April and May. Shaded areas indicate inversion or isothermic conditions. Unshaded areas denote lapse conditions.

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With increasing concentrations of gas, the incidence of occurrence falls off rapidly and the positions of the modes shift. A detailed analysis of the fine structure of the figures is not of sufficient general interest to be included here. However, the concentration class 0·10 p.p.m. or greater should be noted. The modes are all with west

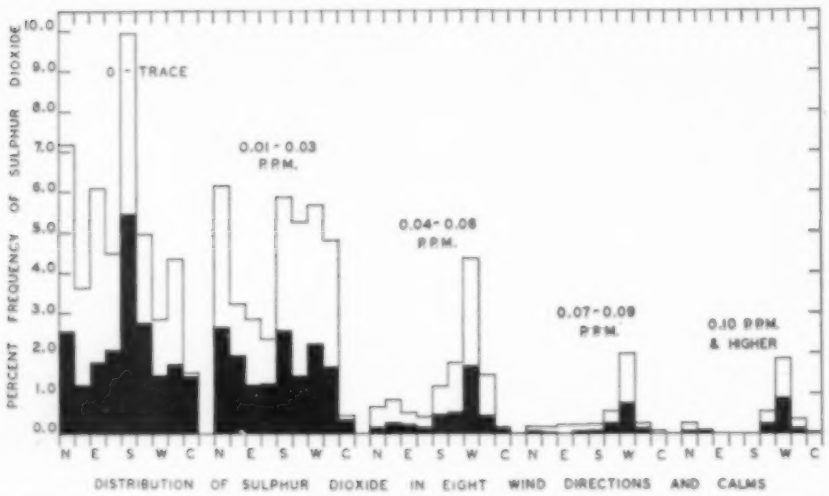
PERCENT FREQUENCY OF SULPHUR DIOXIDE
0 - TRACE
0.01 - 0.03 P.P.M.
0.04 - 0.06 P.P.M.
0.07 - 0.09 P.P.M.
0.10 P.P.M. & HIGHER
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF SULPHUR DIOXIDE IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 4. Percentage frequency histograms of sulphur dioxide concentrations by wind direction for the summer months June, July and August. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions

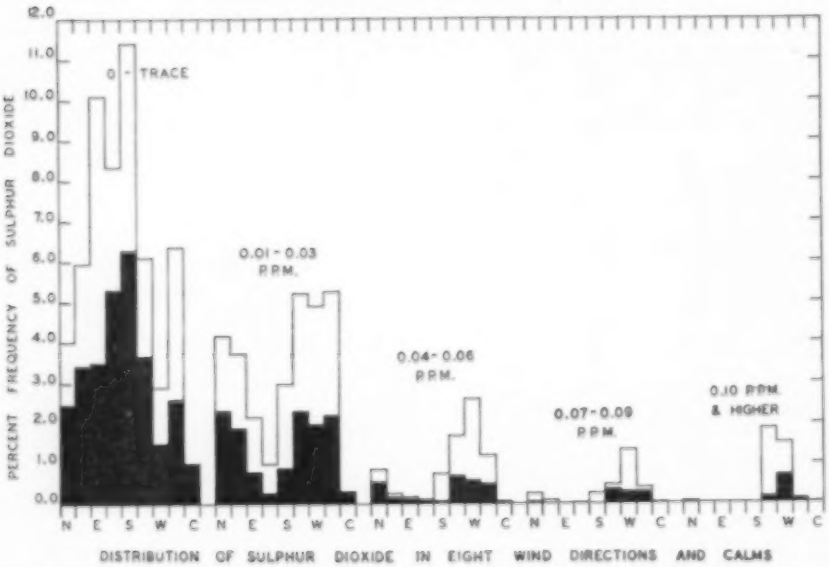
PERCENT FREQUENCY OF SULPHUR DIOXIDE
0 - TRACE
0.01 - 0.03 P.P.M.
0.04 - 0.06 P.P.M.
0.07 - 0.09 P.P.M.
0.10 P.P.M. & HIGHER
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF SULPHUR DIOXIDE IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 5. Percentage frequency histograms of sulphur dioxide concentrations by wind direction for the autumn months September, October and November. Unshaded areas denote lapse conditions.

or southwest winds and occurrences with other wind directions are relatively rare. In other classes, lapse rate appears to have very little effect on the distributions. However, for concentrations of 0·10 or greater, the modes under inversion conditions are all with west winds; in contrast, under lapse conditions they occur mainly with southwest winds. In order to explain the difference, it is necessary to consider Tables 1, 2 and 5.

For winds of 0–4 knots, under lapse conditions, high concentrations of gas are rare, as shown in Table 1, and there are not enough cases to define a mode. Under inversion conditions, there is a mode occurring with north winds. The corresponding time distribution in Table 2 (A) has a peak just before sunrise. This is a little too early in the morning to be associated with an emission increase, if such exists, or with a Hewson fumigation. However, it is not feasible to offer alternative explanations because the data cannot be considered representative of the area when winds are so light.

TABLE 1. PERCENTAGE FREQUENCY DISTRIBUTION OF 584 CASES OF SO_2 CONCENTRATION EQUAL TO OR GREATER THAN 0·10 p.p.m., BY WIND DIRECTION, BY WIND SPEED AND BY LAPSE RATE

	N	NE	E	SE	S	SW	W	NW	Calm	Total cases	% of total
Wind speed 0–4 knots											
Lapse	0·9	0·3	0·5	0·3	0·3	0·0	0·2	0·3	0·2	18	3·1
Inversion	2·2	0·0	0·5	0·2	0·2	0·3	1·5	2·1	0·5	44	7·5
All cases	3·1	0·3	1·0	0·5	0·5	0·3	1·7	2·4	0·7	62	10·6
Wind speed 5–9 knots											
Lapse	2·6	1·2	0·1	0·0	0·8	2·2	4·1	2·4		79	13·6
Inversion	1·0	0·2	0·2	0·2	0·2	2·6	7·7	1·5		79	13·5
All cases	3·6	1·4	0·3	0·2	1·0	4·8	11·8	3·9		158	27·1
Wind speed 10 knots and over											
Lapse	1·5	0·3	0·3	0·0	0·5	29·4	17·4	2·9		307	52·5
Inversion	0·2	0·0	0·0	0·0	0·0	2·1	6·9	0·7		57	9·8
All cases	1·7	0·3	0·3	0·0	0·5	31·5	24·3	3·6		364	62·3

TABLE 2. NUMBER OF CASES BY TIME OF DAY FOR MODES* OF TABLE 1

Wind speed	Direction	Stability	Time, EST						Total
			23–02	03–06	07–10	11–14	15–18	19–22	
(A) 0–4	NW and N	Inversions	2	12	8	2	0	1	25
(B) 5–9	W	Lapse	3	3	13	2	2	1	24
5–9	W	Inversions	14	9	14	1	0	7	45
(C) 10 or higher	SW	Lapse	9	10	31	44	44	34	172
(D) 10 or higher	W	Lapse	6	18	30	10	19	19	102
10 or higher	W	Inversions	7	10	10	1	5	7	40

* Mode is wind direction of greatest frequency for various classes of wind speeds.

For winds of 5–9 knots, under both lapse and inversion conditions, there is a mode with west winds. The corresponding time distributions in Table 2 (B) show a sharp peak just after sunrise, while under inversions there is also a secondary peak about midnight.

For winds of 10 knots and over under inversion conditions, the distributions are quite similar to those with winds of 5–9 knots. However, with lapse conditions, the peak in Table 1 becomes greatly intensified and shifts to southwest. Of the entire frequency distribution, 47 per cent occurs under lapse conditions with southwest or west winds of 10 knots and greater. The time distribution with west winds, Table 2 (D), is similar to that with speeds of 5–9 knots, i.e. a peak just after sunrise. However, for southwest winds, Table 2 (C), the time distribution is quite different—with an afternoon peak.

The westerly peaks occurring shortly after sunrise are associated with emission increases and/or Hewson fumigations. The afternoon southwesterly peak is caused by a looping plume from the J. Clarke Keith steam generating plant, reinforced by emission sources in Zug Island, Ecorse and River Rouge, and associated with thermal and mechanical turbulence. A different analysis of the data will be used in a later section in an attempt to define more clearly the causes of the daily concentration cycle.

It might be argued that Table 1 merely reflects the general frequency distribution of wind speeds. This, however, can be refuted by an examination of Table 5 (percentage of cases in each wind speed and stability class with concentration equal to or greater than 0·10 p.p.m.). It can be seen that even on a relative rather than on an absolute basis, the percentage of high concentrations of sulphur dioxide increases with increasing wind, both under lapse and inversion conditions.

It is clear, therefore, that the SO_2 observations included in this paper are greatly influenced by the location of point sources of emission. The highest SO_2 concentrations at the Peter and Chappell sampling station are associated mainly with unstable air and strong winds, in contrast to the classical " inversion " picture of pollution.

5. VARIATIONS OF SUSPENDED PARTICULATE CONCENTRATIONS WITH WIND

Figs. 6–10 and Tables 3, 4 and 5 display data in a similar fashion to the previously described SO_2 tabulations. However, it is not to be implied that the selected class limits represent equivalent percentiles.

The patterns formed by the shaded histograms show similarities to those of the total histograms. There is also a tendency for the percentage of shaded area to increase with increasing concentration of particulates. For example, on an annual basis in Fig. 6 the ratio of the shaded to the total area is 0·22, 0·27, 0·47, 0·36 and 0·54 in the five concentration classes in ascending order respectively. For the annual SO_2 histograms, on the other hand (Fig. 1), the ratios are 0·26, 0·21, 0·29, 0·28 and 0·31 respectively. This suggests that a different mechanism is operating in the two cases.

In the concentration class 0–0·4 Coh/1000 ft the total histograms display an irregular plateau rather than a clearly defined mode with any wind direction. As concentrations increase, modes begin to appear with west and with north winds. This suggests that the Hemeon smoke sampler is much more sensitive to more distant

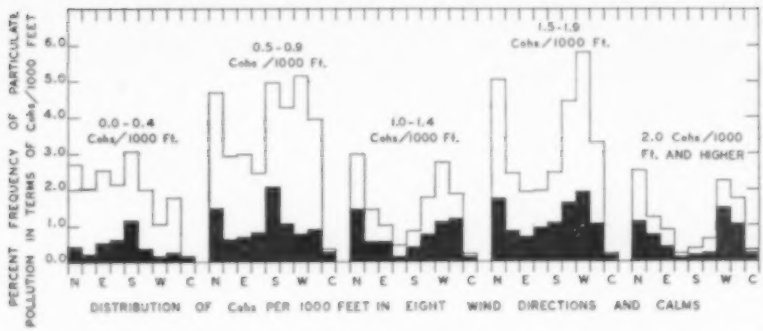
PERCENT FREQUENCY OF PARTICULATE POLLUTION IN TERMS OF Cohs/1000 FEET
0.0-0.4 Cohs/1000 Ft.
0.5-0.9 Cohs /1000 Ft.
1.0-1.4 Cohs/1000 Ft.
1.5-1.9 Cohs/1000 Ft.
2.0 Cohs/1000 Ft. AND HIGHER
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF Cohs PER 1000 FEET IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 6. Percentage frequency histograms of particulate pollution by wind direction on an annual basis. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions.

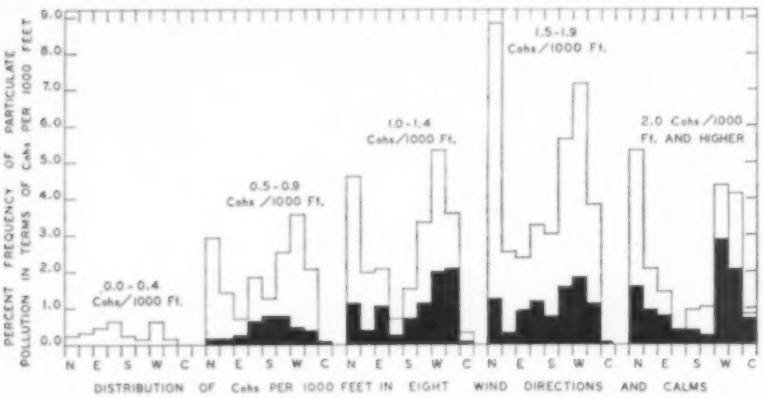
PERCENT FREQUENCY OF PARTICULATE POLLUTION IN TERMS OF Cohs PER 1000 FEET
0.0-0.4 Cohs/1000 Ft.
0.5-0.9 Cohs /1000 Ft.
1.0-1.4 Cohs/1000 Ft.
1.5-1.9 Cohs/1000 Ft.
2.0 Cohs/1000 Ft. AND HIGHER
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF Cohs PER 1000 FEET IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 7. Percentage frequency histograms of particulate pollution by wind direction for the winter months December, January and February. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions.

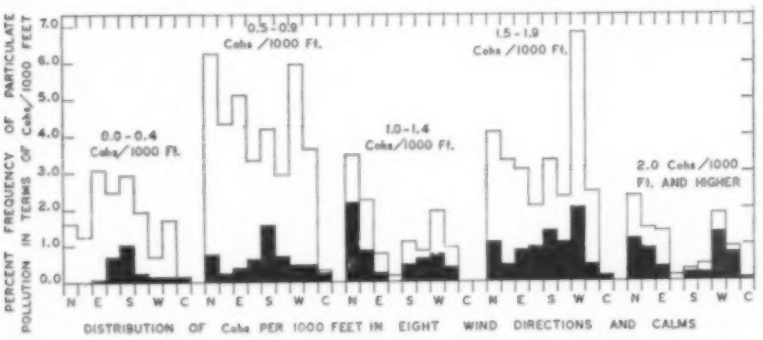
PERCENT FREQUENCY OF PARTICULATE POLLUTION IN TERMS OF Cohs/1000 FEET
0.0-0.4 Cohs/1000 Ft.
0.5-0.9 Cohs /1000 Ft.
1.0-1.4 Cohs/1000 Ft.
1.5-1.9 Cohs /1000 Ft.
2.0 Cohs/1000 Ft. AND HIGHER
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF Cohs PER 1000 FEET IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 8. Percentage frequency histograms of particulate pollution by wind direction for the spring months March, April and May. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions.

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Detroit sources than the SO_2 recorder. In the concentration class of 2·0 Coh/1000 ft or greater, there is no increase in frequency with southwest winds under lapse conditions as was the case with SO_2. The reason for this is to be found in Tables 3, 4 and 5, which display distributions of the 477 cases of Coh values equal to or greater than 2·0.

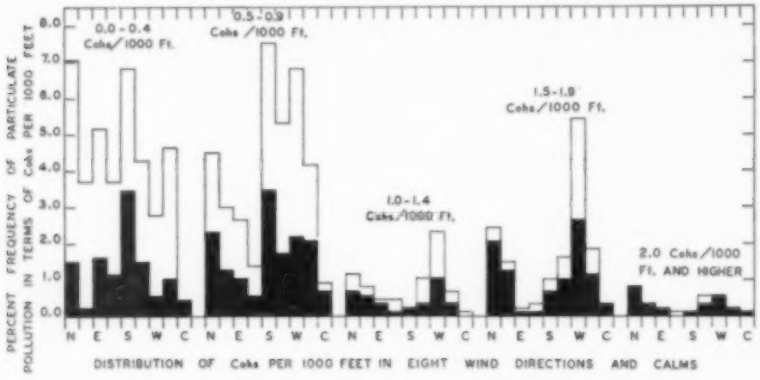
0.0 - 0.4 Cohs/1000 Ft.
0.5 - 0.9 Cohs /1000 Ft.
1.0 - 1.4 Cohs/1000 Ft.
1.5 - 1.9 Cohs/1000 Ft.
2.0 Cohs/1000 Ft. AND HIGHER
PERCENT FREQUENCY OF PARTICULATE POLLUTION IN TERMS OF Cohs PER 1000 FEET
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF Cohs PER 1000 FEET IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 9. Percentage frequency histograms of particulate pollution by wind direction for the summer months June, July and August. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions.

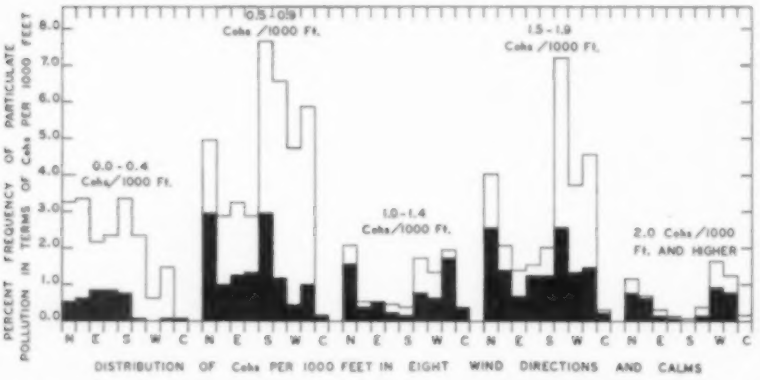
0.0 - 0.4 Cohs/1000 Ft.
0.5 - 0.9 Cohs /1000 Ft.
1.0 - 1.4 Cohs/1000 Ft.
1.5 - 1.9 Cohs /1000 Ft.
2.0 Cohs/1000 Ft. AND HIGHER
PERCENT FREQUENCY OF PARTICULATE POLLUTION IN TERMS OF Cohs PER 1000 FEET
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
N E S W C N E S W C N E S W C N E S W C N E S W C
DISTRIBUTION OF Cohs PER 1000 FEET IN EIGHT WIND DIRECTIONS AND CALMS

FIG. 10. Percentage frequency histograms of particulate pollution by wind direction for the autumn months September, October and November. Shaded areas indicate inversion or isothermal conditions. Unshaded areas denote lapse conditions.

For winds of 0–4 knots, there is a principal mode associated with north winds for both lapse and inversion conditions. The corresponding time distribution in Table 4 (A) indicates a peak number of cases in the period 07–10 EST. The cause is either a Hewson fumigation or the emission cycle.

For winds of 5–9 knots under lapse conditions, the mode is with north winds and the cases are concentrated in the period 07–10 EST. Under inversion conditions, the mode is with west winds, the 8 per cent frequency representing the largest single

TABLE 3. PERCENTAGE FREQUENCY DISTRIBUTION OF 477 CASES OF Cohs/1000 ft EQUAL TO OR GREATER THAN 2·0 BY WIND DIRECTION, BY WIND SPEED, AND BY LAPSE RATE

	N	NE	E	SE	S	SW	W	NW	Calm	Total cases	% of total
Wind 0–4 knots											
Lapse	3·8	1·7	0·9	0·7	0·6	0·4	0·4	0·6	0·8	47	9·8
Inversion	6·7	4·2	2·9	0·8	0·2	0·6	3·6	4·6	2·3	124	26·0
All cases	10·5	5·9	3·8	1·5	0·8	1·0	4·0	5·2	3·1	171	35·8
Wind 5–9 knots											
Lapse	7·0	3·0	3·2	0·4	0·8	0·7	3·3	3·4		103	21·6
Inversion	3·3	3·1	1·0	0·2	1·7	0·8	8·0	4·4		108	22·6
All cases	10·3	6·1	4·2	0·6	2·5	1·5	11·3	7·8		211	44·2
Wind 10 knots and over											
Lapse	3·4	0·0	0·8	0·0	0·4	2·8	3·6	3·1		67	14·0
Inversion	0·8	0·0	0·0	0·0	0·0	0·8	3·1	1·1		28	5·9
All cases	4·2	0·0	0·8	0·0	0·4	3·6	6·7	4·2		95	19·9

TABLE 4. NUMBER OF CASES BY TIME OF DAY FOR MODES OF TABLE 3

	Time, EST						Total
	23–02	03–06	07–10	11–14	15–18	19–22	
(A) Wind speed 0–4 knots N winds							
1—Lapse	1	3	7	5	2	0	18
2—Inversions	5	9	14	1	0	3	32
(B) Wind speed 0–4 knots NW winds							
Inversions	6	10	3	1	0	2	22
(C) Wind speed 5–9 knots NW winds							
Lapse	2	4	15	6	3	3	33
(D) Wind speed 5–9 knots W wind							
Inversions	11	7	11	0	1	8	38
(E) Wind speed 10 knots and over W winds							
1—Lapse	1	2	5	5	1	3	17
2—Inversions	3	2	4	0	0	6	15
(F) Wind speed 10 knots and over N winds							
Lapse	0	0	9	4	3	0	16

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TABLE 5. DISTRIBUTION OF SULPHUR DIOXIDE READINGS AND Cohs/1000 ft BY WIND SPEED AND STABILITY CONDITIONS

	Calm			1–4 knots			5–9 knots			10 knots or greater		
	Total cases	0·1 p.p.m. or higher		Total cases	0·1 p.p.m. or higher		Total cases	0·1 p.p.m. or higher		Total cases	0·1 p.p.m. or higher	
		Number of cases	%		Number of cases	%		Number of cases	%		Number of cases	%
Sulphur dioxide												
Lapse	28	1	3·6	527	17	3·2	3524	79	2·2	4848	307	6·3
Inversion	156	3	1·9	1310	41	3·1	2580	79	3·1	940	57	6·1
		2·0 Cohs/1000 ft or higher			2·0 Cohs/1000 ft or higher			2·0 Cohs/1000 ft or higher			2·0 Cohs/1000 ft or higher	
		Number of cases	%		Number of cases	%		Number of cases	%		Number of cases	%
Cohs/1000 ft												
Lapse	12	4	33·3	181	43	23·8	1143	103	9·0	1755	67	3·8
Inversion	45	11	24·4	459	113	24·6	821	108	13·2	292	28	9·6

inversion or lapse percentage in Table 3. The time-of-day distribution (Table 4 (D)) shows two flat peaks about midnight and in the period 07–10 EST.

For winds of 10 knots or greater, under lapse conditions, there are two small modes with west and north winds. This is very much in contrast to the SO_2 distribution in Table 1, where 47 per cent of the entire frequency occurred under lapse conditions with southwest or west winds of 10 knots or greater.

Under inversion conditions with winds of 10 knots or greater, there is a small mode with west winds, associated mainly with the 07–10 EST period of the day.

Examination of Table 5 reveals that the chance of a high Coh value decreases with increasing wind speed both under lapse and inversion conditions. This is again in contrast with the SO_2 results (Table 5).

The evidence suggests that Coh values are a much more reliable index of the general levels of pollution in the metropolitan area than are SO_2 readings. Although the position of emission sources with respect to the sampling station has some effect on the concentration of suspended particulates, the influence is much less than in the case of sulphur dioxide. It is believed that the Coh value results at the Peter and Chappell sampling station are representative, on a relative basis, of the southern metropolitan area, i.e. of the City of Windsor. This is supported by previous studies with networks of high volume samplers (INTERNATIONAL JOINT COMMISSION, 1959). Exceptions do, of course, occur when there are very local sources of smoke such as the railroad roundhouse. By " on a relative basis " is meant that concentrations of suspended particulates at other locations in Windsor would show good correlation with the Peter and Chappell data. It would be quite natural to expect certain differences for a sampling point in the north part of Detroit, e.g. larger frequencies of high concentrations with south and southeast winds.

6. THE DAILY CYCLE OF SULPHUR DIOXIDE POLLUTION

Figs. 11–15 depict the relevant features of the daily cycle of SO_2, on an annual and on a seasonal basis. The divisions of the day marked 1–6 represent 4-hr periods corresponding to the times 23–02, 03–06, 07–10, 11–14, 15–18, and 19–22 EST respectively. Cumulative frequencies have been used, and the ordinate is on a

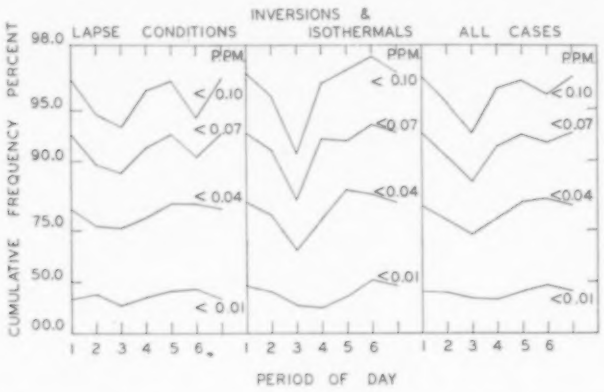

FIG. 11. Cumulative percentage frequency, on a logarithmic scale, of sulphur dioxide concentrations by period of the day on an annual basis.

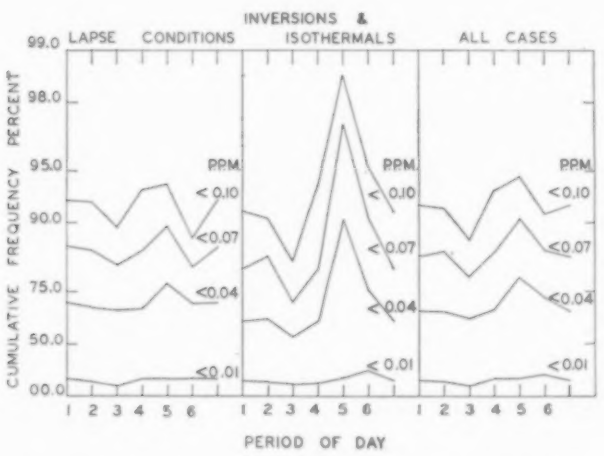

FIG. 12. Cumulative percentage frequency, on a logarithmic scale, of sulphur dioxide concentrations by period of the day for the winter months December, January and February.

logarithmic scale in order to emphasize the higher concentration classes. A dip in the curves corresponds to a relatively large number of occurrences of high concentrations; a peak indicates a deficit. Each figure contains three parts—a plot of the entire sample and of lapse and inversion cases separately.

The figures indicate a well-marked mean daily cycle, the significant features of which may be summarized as follows:

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(a) *All cases*

On an annual basis (Fig. 11) there is a surplus of high concentrations in the period 07–10 EST, with a small secondary surplus in the evening (19–22 EST). The cycle is very similar to results reported elsewhere in the United States (IVES, 1936) and in Great Britain (DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH, 1945). It is

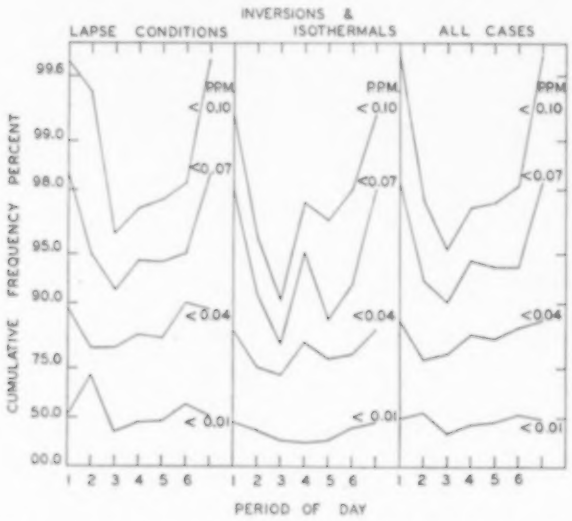

FIG. 13. Cumulative percentage frequency, on a logarithmic scale, of sulphur dioxide concentrations by period of the day for the spring months March, April and May.

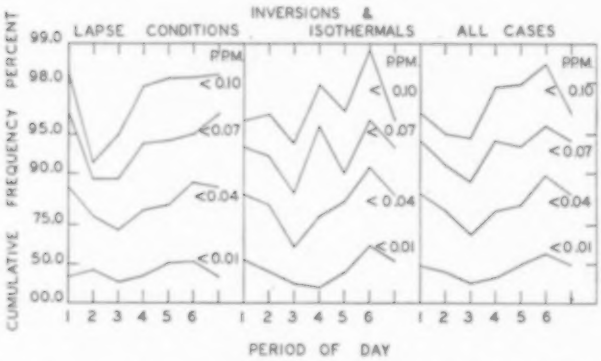

FIG. 14. Cumulative percentage frequency, on a logarithmic scale, of sulphur dioxide concentrations by period of the day for the summer months June, July and August.

seen in Figs. 12–15 that the morning surplus persists through all four seasons. The evening surplus is present in the winter; in the spring and autumn it occurs at a lower concentration level (0·07 in the spring and 0·04 in the fall, while the 0·10 curve shows only a change in slope); in the summer the effect has either disappeared or has shifted to the time period 15–18 EST and concentration level 0·07.

(b) *Lapse cases*

The morning surplus occurs in all four seasons. However, during the summer months the time of occurrence is earlier—in the period 03–06 EST. The evening surplus is clearly marked on an annual basis and in the winter and autumn (including later data from the autumn of 1957, which is not displayed). In the spring and summer it disappears.

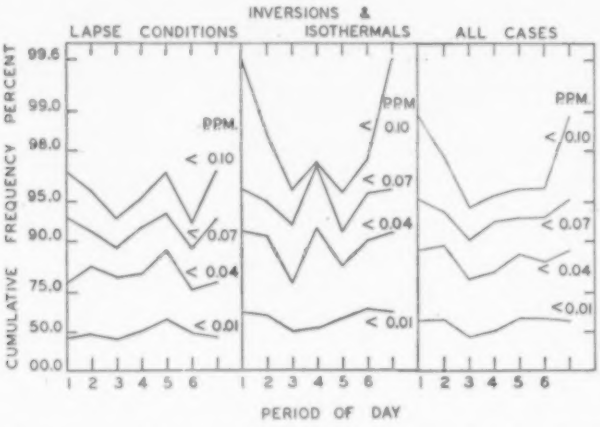

FIG. 15. Cumulative percentage frequency, on a logarithmic scale, of sulphur dioxide concentrations by period of the day for the autumn months September, October and November.

(c) *Inversion cases*

The morning surplus again occurs in all four seasons in the time period 07–10 EST. On an annual basis, and in the winter, the evening secondary is not present. In the spring, summer, and autumn, there is a late afternoon surplus (15–18 EST); even this is not present in the additional data (not displayed) for the autumn of 1957.

7. THE DAILY CYCLE OF SUSPENDED PARTICULATE CONCENTRATIONS

Figs. 16–20 show relevant features of the daily cycle. Certain points have been omitted from Figs. 18–20 for two reasons:

(1) The selected type of graphical display will not tolerate a cumulative frequency of 100 per cent—a point at infinity. For example, in the summer season, total sample, during the period 11–14 EST, there were 131 cases but not one exceeded a concentration of 2·0. It is presumed that a larger 5 or 10 yr sample would have overcome this difficulty.

(2) The type of expanded logarithmic scale is not justified if the number of cases is small; this situation occurred under inversion conditions during the afternoon, and also during the summer under lapse conditions at night.

It is believed that the points that have been included form a pattern that is significant on a relative, but not necessarily on an absolute basis. The figures indicate a well-marked daily cycle, the significant features of which may be summarized as follows:

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(a) *All cases*

On an annual basis and in all seasons except summer, the morning surplus of high concentrations in the period 07–10 EST is well marked, and in this respect the curves are similar to those for SO_2. However, during the summer months the time of the mode for high Coh values is shifted—to 23–02 EST for the concentration level 2·0

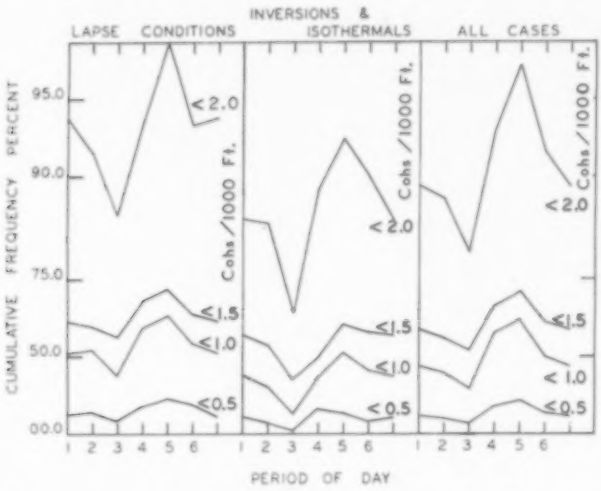

FIG. 16. Cumulative percentage frequency, on a logarithmic scale, of particulate pollution by period of the day on an annual basis.

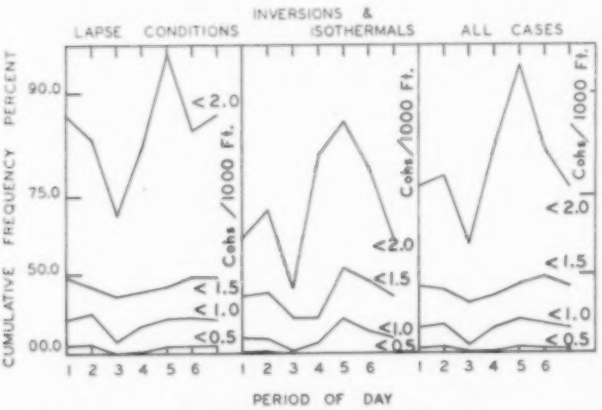

FIG. 17. Cumulative percentage frequency, on a logarithmic scale, of particulate pollution by period of the day for the winter months December, January and February.

and to 03–06 EST for the level 1·5. The evening features of Figs. 16–20 are quite different from those of Figs. 11–15. On an annual basis, and in spring and summer, the Coh values have no secondary mode of high concentrations. In the winter, there is a small surplus in the period 23–02 EST; in the autumn it appears in the period 19–22 EST.

(b) *Lapse cases*

The morning surplus occurs at the regular time (07–10 EST) in all seasons plotted. The evening secondary is persistent through the set of curves and shows no seasonal time shift, occurring in the period 19–22 EST. However, it is at a lower concentration level (1·5) in the winter than in other seasons.

(c) *Inversion cases*

The morning surplus occurs at the regular time (07–10 EST) in all seasons plotted. There is no secondary evening mode except in winter during the period 23–02 EST.

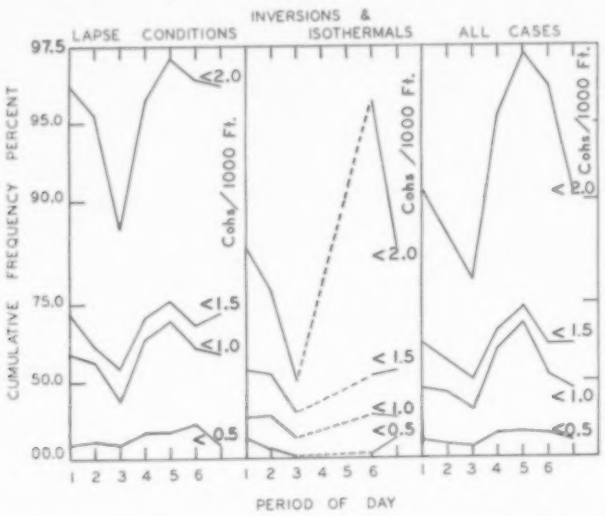

FIG. 18. Cumulative percentage frequency, on a logarithmic scale, of particulate pollution by period of the day for the spring months March, April and May.

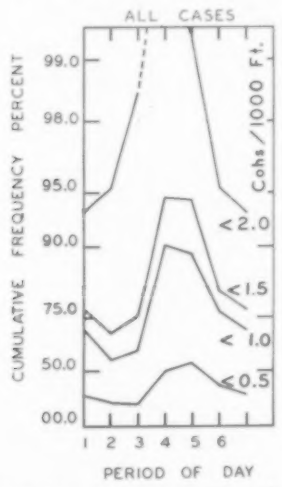

FIG. 19. Cumulative percentage frequency, on a logarithmic scale, of particulate pollution by period of the day for the summer months June, July and August.

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The main features of Figs. 11–20 having been identified, it would be desirable to consider physical explanations. However, the annual curves (Figs. 11 and 16) do not readily yield their secrets because they are a composite of large seasonal differences. It is therefore necessary to delay discussion until other data are introduced in the following section.

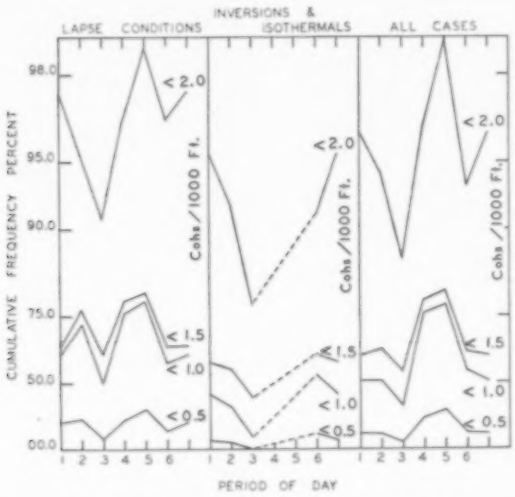

FIG. 20. Cumulative percentage frequency, on a logarithmic scale, of particulate pollution by period of the day for the autumn months September, October and November.

8. SEASONAL CYCLES OF POLLUTION

The seasonal distribution of pollution without regard to weather factors is given in Table 6. For sulphur dioxide, the spring and summer percentages are similar. In the autumn, there is an increase in the class 0-trace at the expense of the next two classes. In winter, the median concentration level is considerably higher than at any other time of the year.

For Coh values, the lowest median concentration level occurs in summer, while the highest is in winter. Spring and autumn appear to be transition periods between the two extremes. The seasonal variation is much larger for Coh values than for SO_2, both on an absolute and on a relative basis.

In winter, mean wind speed is at a maximum and inversion frequencies are at a minimum; yet concentration levels for both SO_2 and Coh values are at a maximum. Since the meteorological mechanisms are different for the two forms of pollution (as shown earlier), it follows that emissions (at a maximum in the winter) must be the controlling factor in the resulting general levels of pollution. Another possible explanation, a seasonal shift in wind direction frequencies that fortuitously results in a winter maximum of high concentrations of both SO_2 and suspended particulates, has been examined and found inadequate. The detailed analysis is too lengthy to be included here; however, the magnitude of seasonal variations in wind direction is given in Table 7. It is emphasized that Table 7 is not intended to represent long-term climatic averages; instead it is included to show seasonal variations within the sample.

Since the seasonal variation in Coh values is greater than for SO_2, it follows next that emissions of SO_2 reaching the sampling station are much steadier throughout the year than are emissions of suspended particulates. This suggests that the sulphur dioxide is coming mainly from industrial or power plants that have modern stack-

TABLE 6. SEASONAL FREQUENCY DISTRIBUTION OF POLLUTION

	Dec.–Feb. %	Mar.–May %	June–Aug. %	Sept.–Nov. %
Sulphur dioxide (p.p.m.)				
0–trace	19·5	45·6	45·0	60·1
0·01–0·03	50·8	38·2	36·7	26·3
0·04–0·06	14·9	10·3	11·4	6·7
0·07–0·09	6·6	3·5	3·8	3·4
0·10 and greater	8·2	2·3	3·2	3·5
Total	100·0	99·9	100·1	100·0
Coh values/1000 linear ft				
0·0–0·4	2·9	15·9	38·6	18·9
0·5–0·9	16·4	36·0	36·3	39·0
1·0–1·4	23·4	11·4	7·3	9·4
1·5–1·9	36·7	27·7	14·8	26·9
2·0 and greater	20·6	9·9	3·1	5·8
Total	100·0	100·0	100·1	100·0

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TABLE 7. WIND DIRECTION IN PERCENTAGE FREQUENCY BY SEASON FOR TOTAL SO_2 SAMPLE

	N (%)	NE (%)	E (%)	SE (%)	S (%)	SW (%)	W (%)	NW (%)	C (%)	Total (%)
Dec., Jan., Feb.	20	7	8	6	8	14	20	15	1	99
Mar., Apr., May	17	12	12	8	13	10	16	11	1	100
June, July, Aug.	14	8	10	7	17	13	17	11	2	99
Sept., Oct., Nov. 1955–56	9	10	12	9	15	15	14	13	1	98
Sept., Oct., Nov. 1957	16	9	7	7	13	19	12	16	1	100

cleaning equipment for the removal of particulates. The suspended soot, on the other hand, is mainly from other sources such as domestic heating.

A surprising feature of Table 6 is the cleanliness of the air during the autumn, in view of the extensive literature relating serious pollution situations with that time of the year. One particular anomaly, the 60 per cent frequency of SO_2 in the class 0-trace, is noted. This is not a peculiarity of one particular year; in the 1955 and 1956 combined autumn data, the frequency was 56 per cent while in the autumn of 1957 it was 65 per cent, both figures well above the summer frequency of 45 per cent. A comparison of the patterns of histograms in Figs. 1 and 5 in the class 0-trace reveals that the increase is due entirely to the increase in autumn shaded areas; under lapse conditions (light areas), there is very little change. This suggests that SO_2 is coming mainly from elevated sources and is not readily reaching ground level under inversion conditions.

Application of the same reasoning to suspended particulates invites the query as

to why the spring and autumn distributions in Table 6 are so similar. Spring is a time of relatively strong winds and of relatively long hours of daylight. When a nocturnal inversion forms in the spring, it persists on the average about $11\frac{1}{2}$ hr, as compared to 15 hr in the autumn. An explanation may be found through consideration of degree day totals. The Detroit City Airport normals are 1736 degrees for March–April–May, and 1224 degrees for September–October–November. Hence, domestic heating requirements and resulting emissions are greater in March–May than in September–November. This factor is approximately equivalent to the seasonal difference in climatic parameters.

Although the autumn is traditionally the season for stagnant warm anticyclones in the Eastern United States, there are also periods, particularly as far north as Detroit, when fresh polar anticyclones follow one another in rapid succession with good ventilation and little accumulation of pollution. Certainly many a clear October day shows no visible sign of particulates. The autumn frequencies in Table 6, therefore, reflect a composite picture drawn from differing synoptic patterns.

9. RECONSIDERATION OF FIGS. 2–5 AND 7–10

If the indirect reasoning of the previous section is accepted (establishing qualitatively an annual cycle in emissions), then it is possible to explain the seasonal differences in Figs. 2–5 and 7–10. The complete analysis requires a study of the annual cycles of the meteorological parameters and is lengthy. Only two examples will be described here, both from Figs. 2–5, concentration class of SO_2 equal to or greater than 0·10 p.p.m.

(a) In winter, spring and summer, the mode for all cases is with west winds; in autumn it is with southwest winds. Why? Table 7 suggests that the shift in the mode may be attributed to an increase in frequency of southwest winds in autumn. The additional September–November 1957 data (not included in Fig. 5) support this conclusion, as indicated below:

	% Frequencies (from Table 7)		% Frequencies of $SO_2 \geq 0{\cdot}10$ p.p.m.	
	SW	W	SW	W
September–November 1955/56	15	14	1·9	1·5
September–November 1957	19	12	2·5	0·8

The increased frequency of southwest winds in 1957 resulted in a strengthening of the mode with southwest winds.

(b) Under lapse conditions there is a mode with southwest winds in fall, winter and spring. Why is there not a mode in summer? The frequency of southwest winds in summer (Table 7) is not too different from other seasons, so the explanation must be found elsewhere.

Another possible factor is wind speed. Table 1 shows that most cases of high sulphur dioxide concentrations occur with winds of 10 knots or higher. Furthermore, winds are lighter in summer than in winter. However, the actual frequency of southwest winds of 10 knots or greater proved to be 4·7 per cent for the summer and

7·0 per cent for the remainder of the year. This was not a sufficiently large difference to explain the anomaly.

Another trial hypothesis is that 10 knots is not a critical wind speed; the number 10 was merely chosen for convenience of IBM programming. Perhaps the real value is sufficiently high to exclude nearly all summer cases. A logical extension of the analysis is, therefore, displayed in Fig. 21. In view of the distance of the wind observation site at Detroit City Airport from the sampling station, the authors are surprised at the sharp contrasts obtained.

Consider first the heating season curve. In the lower wind speeds (10–13 knots) there were sufficient cases to plot separate points for each nautical mile of wind. In

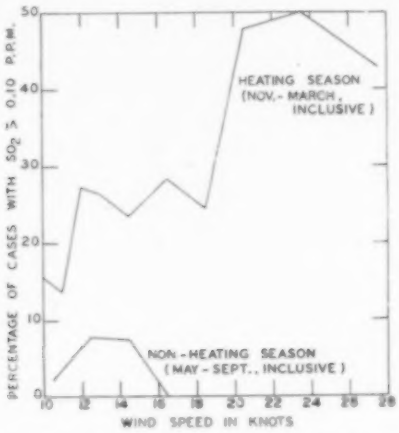

FIG. 21. Relation between wind speed and relative frequency of the higher concentrations of sulphur dioxide in the heating and non-heating seasons of the year.

the upper wind speeds, it was necessary to group; however, the last three points represent sufficient cases (65) to portray a significant trend. The curve is characterized by two sharp rises in frequency—one between 11 and 12 knots and the other at about 20 knots.

The technician who regularly visits the sampling station has observed that with very strong winds a plume of SO_2 curls down the edge of the lee side of the J. Clarke Keith steam generating plant and proceeds towards the sampling station at ground level. This effect is explained physically by the turbulent vortex that forms in the wake of an obstruction; it is often called " downwash " to distinguish it from looping. In this case, the critical downwash speed is about 20 knots. On the other hand, the critical speed for the looping plume, which clears the generating plant but reaches ground level later in puffs, appears to be 12 knots.

The non-heating season curve displays an entirely different character. In the first place, the curve could not be extended to 20 knots because of insufficient cases. Secondly, the upper plotted point represents a total sample of 24, and yet there was not one occurrence of an SO_2 concentration of 0·10 p.p.m. or greater. (This is also true of the additional few cases with winds of 20 knots or more.)

In the wind speed range of 10–19 knots, there is a marked reduction in frequency of high concentrations in the non-heating season. Since the comparison is on a

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relative basis, it cannot be explained by the lower frequency of strong southwest winds in summer, but must reflect decreased activity of the generating plant at that time of year. A contributing factor might be a seasonal variation in eddy structure near the ground. Superimposed upon mechanical turbulence is thermal turbulence, which is likely to have a different character in summer than in winter. It is not possible to investigate this factor with the available data.

In the non-heating season there is again an increase in frequency at about 12 knots. This suggests that the 12 knot value is a critical limit for the looping plume at all times of year.

In summary, the lack of a summer southwest mode is caused jointly by a reduction of activity at the steam generating plant and by a reduction in frequency of winds of 12 knots or greater.

10. THE MORNING PEAK IN THE DAILY POLLUTION CYCLE

Consider first the morning surplus of high concentrations of sulphur dioxide (Figs. 11–15). It is required to determine whether this is due to the daily emission cycle or to the fumigation effect. In the " all cases " curves the surplus occurs in the period 07–10 EST in all four seasons. It is present at all four concentration levels and is, therefore, not particularly associated with the looping plume. This inference is supported by the data in Table 2 (C); high concentrations with unstable southwest winds occur mainly in the afternoon.

Under lapse conditions the morning surplus appears at the regular time except during the summer when it occurs in the period 03–06 EST at the two upper concentration levels. The Detroit–Windsor area remains on standard time throughout the year; therefore, there is no summer shift in the time of the usual morning increase of industrial and domestic activity. This suggests that the phenomenon is related to meteorological factors. Supporting evidence is found by comparing the relatively small morning dip in the winter lapse curves with the relatively large dip in summer. There is no reason to believe that the range of the daily emission cycle would be smaller in winter than in summer. However, the frequency of Hewson fumigations is indeed less. In winter, lapse conditions persist quite frequently throughout the night, but in summer, nocturnal inversions are the rule (72 per cent in summer as compared with 36 per cent in winter in the period 03–06 EST).

Sunrise occurs at about 5 a.m. through June and most of July, in contrast to 8 a.m. on 1 January. In the summer, therefore, the period 03–06 EST includes approximately 1 hr of daylight, sufficient time for a fumigation on many occasions.

Under inversion conditions, the morning surplus of high SO_2 concentrations appears in the period 07–10 EST at all times of year. It has already been established that the sulphur dioxide reaching the sampling station originates mainly from elevated sources and that diffusion of the gas to ground level under inversion conditions occurs only with difficulty. A morning increase in emissions would, therefore, not in itself cause the surplus under inversion conditions.

It is suggested that the anomaly can again be explained by the fumigation effect. This is supported by the following arguments:

(a) The layer of air used to define lapse rate conditions is from 20 to 300 ft. The nocturnal inversion disappears first at ground level, the fumigation gradually building up to 300 ft. The inversion set of curves, therefore, includes morning cases in which lapse

conditions have already developed but have not extended upwards as far as 300 ft.

(b) The time of inversion break-up at the television tower does not coincide exactly with the time at the sampling station.

Although valid reasons have been given for the morning surplus under inversion conditions, it is still necessary to explain why there is no summer shift in time as in the case of the lapse curves. The possibility of a statistical sampling error is unlikely because a similar summer effect occurs with suspended particulates in Fig. 19.

A reasonable explanation can be given for sulphur dioxide in terms of cumulative effect. Summer lapse cases during the period 03–06 EST will contain fumigation observations. On days of such occurrences, and in the next 4-hr period, 07–10 EST, the ground-level concentrations of gas will be relatively low as a result of continued vigorous eddy action. Hence, as the morning proceeds, the relative frequency of high ground-level concentrations under lapse conditions will decrease. With inversions, on the other hand, there is no increasing accumulation of low concentration cases caused by fumigations at an earlier hour. Instead, the chance of a fumigation under inversion conditions increases as the morning hour becomes later.

Consider next the morning peak of suspended particulate matter as illustrated in Figs. 17–20. In all seasons except summer it is well marked in the period 07–10 EST. Unfortunately, there are insufficient summer observations to separate lapse from inversion conditions. However, the available evidence in Fig. 19 suggests that the surplus occurs at an earlier hour. In the case of the 2·0 Coh/1000 ft curve, there is a shift of two periods to 23–02 EST and this cannot be explained by the available data. For the 1·5 and 1·0 curves, the surplus is in the period 03–06 EST, the explanation of which parallels that given in the case of sulphur dioxide (a fumigation rather than an increase in emission).

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11. THE EVENING PEAK IN THE DAILY POLLUTION CYCLE

A secondary evening surplus of high concentrations is well documented throughout the air pollution literature. However, as yet no satisfactory explanation has been offered. It is believed that the present study is the first attempt to examine the effect on a seasonal basis and in relation to lapse rates.

With respect first to Figs. 12–15, why is there a surplus of high sulphur dioxide concentrations under lapse conditions in the autumn and winter, but not in the spring and summer? The surplus is not caused by an evening increase in emissions; otherwise, there would be a similar effect in spring, which has a higher degree day total than autumn. Furthermore, the surplus is not the result of a looping plume which has a maximum frequency in the afternoon (Table 2) and which occurs in spring as well as in winter and autumn.

It has been established that sulphur dioxide emissions are mainly from elevated sources. Decreasing late afternoon and evening turbulence can, therefore, hardly explain the effect. Eddy activity diminishes first near ground level, gradually extending upwards and producing " lofting ", a condition in which the pollution is free to escape aloft but has difficulty in reaching ground level.

The authors are, therefore, led to the hypothesis of an evening fumigation mechanism in which there is eddy activity near the ground with stable air aloft. Such a theory would appear at first glance to be rather difficult to substantiate but must be given careful consideration. Four possible mechanisms will be discussed:

(1) In the evening, thermal turbulence may have disappeared while mechanical turbulence remains in the lowest 100 ft or so. Such an explanation is unsatisfactory because the evening pollution peak does not occur under inversion conditions and is not present in the spring.

(2) The heat of fusion, when water changes to ice, may warm the air and produce an adiabatic profile near the ground, destroying, in the very lowest layers, an inversion that has developed to considerable height. Such an effect might be present in the autumn and winter; however, in a large sample of data, it is not likely to occur predominantly in a specific time period, 19–22 EST. If there were any clustering of cases, the mode would be somewhat earlier in the winter than in the autumn.

(3) Precipitation can modify an inversion, changing it to a saturated adiabatic profile. An evening fumigation could, therefore, conceivably be caused by precipitation falling through a well-established ground-level inversion. In order to explore the possibility, however, it would be necessary to examine the diurnal and seasonal patterns of precipitation, a study beyond the scope of this paper and to be reported later.

(4) When meteorological conditions are right, inversions develop over rural areas. However, heat sources in the city, including automobile exhaust gases (WHITEN, 1956), maintain lapse conditions in the very lowest levels throughout the urban area. DUCKWORTH and SANDBERG (1954) have observed the phenomenon with simultaneous wiresonde ascents over built-up and open areas. A complex city " heat-island " circulation may develop, resulting in stable air aloft and instability near the ground in the vicinity of industrial areas, expressways, etc. In Bath, England (BALCHIN and PYE, 1947), for example, small cumulus-like clouds were observed on one or two occasions over the centre of the city when there was fog on the outskirts.

Sulphur dioxide is emitted mainly from sources at heights of 200 to 300 ft. Hence, the heat-island hypothesis requires a stable layer of air at about 300 ft with lapse conditions below. Since the evening pollution peak occurs only under lapse conditions (in the 20 ft–300 ft layer), the theory demands that the WJBK Television Tower site be within the heat-island in autumn and winter and that there be some evidence of inversion conditions in the upper levels.

Evidence for upper inversions is incomplete because the 600 ft temperatures were unreliable until October 1956. However, the percentage of cases in each 4-hr period in winter with concentrations less than 0·10 p.p.m. was as follows:

Time of day (EST)	23–02 %	03–06 %	07–10 %	11–14 %	15–18 %	19–22 %
All lapse cases (data plotted on left-hand side of Fig. 12)	93	92	89	94	94	88
Lapse cases with inversions aloft	88	86	83	93	*	69

* Insufficient cases.

The samples are not drawn from the same population, and, therefore, the results are not in any sense conclusive. However, the evidence suggests that something unusual is taking place in the period 19–22 EST and that the evening surplus of high

concentrations is accentuated when there is a fumigation situation. It is planned to investigate this at a later date when more data are available.

In the case of suspended particulates under lapse conditions, there is a peak in the period 19–22 EST but it occurs in the spring as well as in autumn and winter. Another feature not present in the SO_2 curves is the winter and annual inversion peak in the period 23–02 EST. If the evening fumigation hypothesis is accepted, then ground-level turbulence is required to extend upwards only to 50 or 100 ft for suspended particulates because of the generally lower sources of emission. Presumably the effect can, therefore, occur more frequently, a reason for its presence in more seasons of the year than in the case of sulphur dioxide.

The separation of data in this study is based upon whether the 20 ft–300 ft temperature difference is positive or negative. In the evening, any inversion in the upper part of the layer is likely to be slight, which would account for the evening pollution peak under tabulated lapse conditions. The argument may be extended to explain the later peak (23–02 EST) under inversion conditions in Figs. 16 and 17; it is perhaps due to the fact that the inversion in the upper part of the 20 ft–300 ft layer requires time to develop sufficiently to outweigh the lower lapse conditions in the tabulations.

The principal objection to a " heat-island " hypothesis is that the WJBK Television Tower site is rather far from downtown Detroit. DUCKWORTH and SANDBERG (1954) suggest 4–6 miles² as the significant central area for San Francisco. The authors of the present paper would welcome more published data from other cities.

There remains to be explained an SO_2 surplus under inversion conditions in the 15–18 EST period in the spring, summer and fall. This is a daytime phenomenon and it is necessary to consider under what conditions there might be a net inversion in the 20–300 ft layer in the afternoon. Preliminary investigation suggests occurrence in the wake of precipitation, possibly as a result of surface evaporational cooling. A detailed analysis is beyond the scope of the present paper.

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12. CONCLUSION

Ground-level concentrations of pollution are a function of emissions and of meteorological factors. On any one day, the concentrations may show very irregular variations, and it is only when large samples of data are considered that well-defined daily and seasonal patterns emerge. Using an IBM punch-card system, it has been possible to analyze the patterns in the Detroit–Windsor area. The results of the study are given in some detail in the abstract and will not be reported here.

A 2-yr sample of data has been used and the emphasis has been placed on the relationships within the sample. No attempt has been made to define climatic norms. However, it is believed that when more data are accumulated, it will be possible to specify conditional probabilities for pollution prediction. Given the time of day, month of year, wind direction, wind speed and lapse rate, the probability of concentrations falling within designated class limits can be stated for the Peter and Chappell station. With sufficiently broad class limits, and in the case of suspended particulates, the probabilities can be used as an index for a large part of the Detroit–Windsor area. Sulphur dioxide records, on the other hand, although of great value in single stack studies, are not particularly representative of the larger environment.

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THE AIR POLLUTION BY WASTE GASES FROM FACTORIES IN THE INDUSTRIAL AREA OF TOKYO

S. ICHIKAWA, G. URAKUBO and N. YAMATE
National Hygienic Laboratory, Tokyo, Japan
(*Received* 2 *November* 1958)

Abstract—A survey of the concentration of air pollutants from chemical factories has been carried out in three selected industrial areas. In factories where preventive measures were either absent or inadequate, concentrations of SO_2 and NO_2 were respectively in the ranges 0·016–0·80 p.p.m. and 0·04–16 p.p.m. In the surrounding districts the SO_2 concentration was in the range 0·01–0·37 p.p.m.

INTRODUCTION

THE following report describes part of an investigation of air pollution by waste gases from chemical factories in the industrial area of Tokyo. The districts considered in this survey were suggested by the Public Health Division, Health Bureau of the Tokyo Metropolitan Office, by whom many complaints had been received from local inhabitants. The area around and within the factories was investigated from June to September 1957.

The areas investigated are described below.

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Area A

2-Chome, Chogo-Machi, Itabashi-Ku, where many factories are situated. In this area the principal factory (*S*), which covers approximately 82,000 m², produces

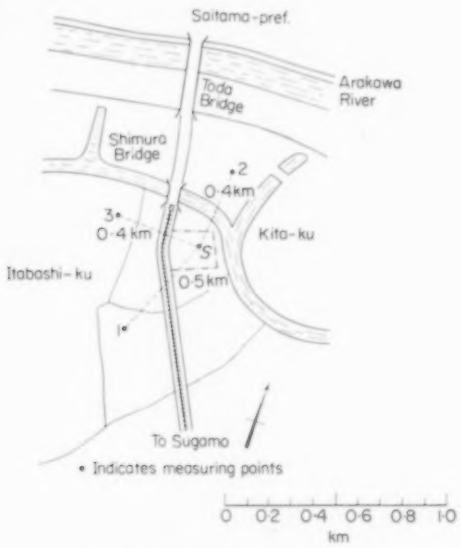

FIG. 1. Sketch map of Area A.

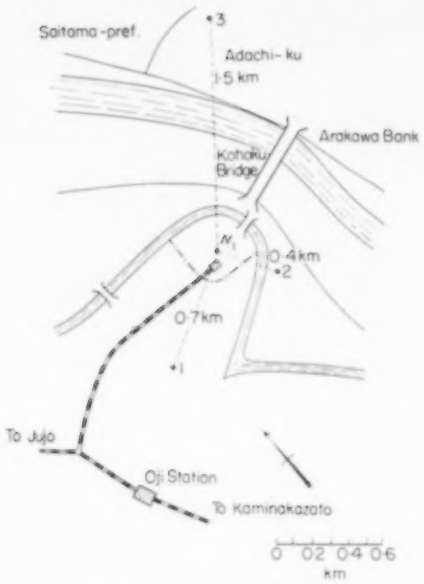

FIG. 2. Sketch map of Area B.

FIG. 3. Sketch map of Area C.

mainly chemical fertilizer and refined nickel. In the nickel refining process, extraction of the residual solution of nickel electrolyte with H_2SO_4 produces large amounts of SO_2. There is always associated with this process a foul smell which at times causes irritation. In the vicinity of this factory there are shops, schools and domestic dwellings.

Area B

5-Chome, Toshima, Kita-Ku. In this district there are many factories of which the chief factory (N_1), covering approximately 230,000 m², produces sulphuric acid and chemical fertilizer. Sulphuric acid is manufactured by the catalytic process and the lead chamber process, both of which cause pollution of the air by sulphur dioxide. In addition there are shops, schools and domestic dwellings in this area.

Area C

Numerous factories are situated around 7-Chome, Oshima-Cho, Koto-Ku, 1-Chome, Komatsugawa and Edogawa-Ku. Three factories were chosen for investigation.

TABLE 1. AREA A

Measuring point	Measuring date	Sampling time	SO_2 (p.p.m)	Weather condition				Remarks
				Temp. (°C)	Humidity (%)	Direction of wind	Velocity of wind (m/sec)	
S	6.6.57	10.40–11.40	0·73	28	61	S	0·7	Severe odour; very irritating strong smell
		12.00–13.00	0·156	29	61	SSE	3·2	
		13.00–14.00	0·800	30	61	S	3·2	
1	4.6.57	10.10–13.20	—	25	70	N	2·6	Factories in the vicinity sometimes smell of smoke and fertilizer
		13.20–16.30	—	27	64	SE	5·0	
	19.6.57	10.15–13.15	—	27	60	SSE	4·4	As above
		13.20–16.30	—	29	53	S	4·4	
2	10.6.57	10.15–13.15	0·154	23	60	S	4·2	Very severe irritating odour
		13.20–16.40	0·133	22	54	S	4·6	
	11.6.57	10.15–13.15	—	21	55	E	3·8	Odourless
		13.30–16.40	—	23	56	E	4·6	
3	12.6.57	10.20–13.00	—	21	81	NNW	3·4	On the roof of an ink factory with smoking chimneys
		13.00–16.30	—	20	89	SE	4·8	
	13.6.57	10.30–13.30	0·015	25	64	NNW	1·7	As above
		13.35–16.30	0·042	28	55	SSE	3·0	

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Factory *P* produces sulphuric acid by the catalytic process.

Factory *T* manufactures chemical fertilizer and sulphuric acid by the catalytic and by the lead chamber processes.

Factory N_2 produces chemical fertilizer and sulphuric acid by the lead chamber process.

In addition there are workshops and hostels, but only a few private houses. Many complaints about the irritating odours have been received from the local residents.

ANALYTICAL METHODS

SO_2 was measured by the fuchsin-formaldehyde method as approved by the Air Testing Conference of the Japanese Pharmacological Association. NO_2 was measured by the sulfanylamide–naphthylethylenediamine method, approved by the Air Testing Conference as above.

Weather conditions were assessed using an Assmann's aspiratory psychrometer and an anemometer after the method approved by the Air Testing Conference.

RESULTS

The results are summarized in Tables 1, 2 and 3.

Table 2. Area B

Measuring point	Measuring date	Sampling time	SO_2 (p.p.m)	Weather condition				Remarks
				Temp. (°C)	Humidity (%)	Direction of wind	Velocity of wind (m/sec)	
N_1	20.6.57	10.10–13.00 13.00–16.00	0·016 0·020	26 29	74 62	ESE SSE	2·6 5·0	Slight smell
1	21.6.57	10.15–13.05 13.10–16.10	0·009 0·012	28 29	66 63	E E	7·8 10·5	Sometimes smell of smoke soap factory NE 200 m
	22.6.57	10.00–13.00 13.10–16.10	— —	26 28	63 50	ENE ENE	1·7 3·8	As above
2	24.6.57	10.10–13.10 13.10–16.15	— —	19 23	60 65	NNE N	1·5 3·8	Many factories in the area, but odourless
	25.6.57	9.30–12.40 12.50–16.00	— —	25 28	58 61	NNE ESE	3·4 3·0	As above
3	26.7.57	9.50–12.45 13.00–16.00	— —	24 24	71 71	N ENE	4·0 7·8	Farm area odourless
	23.7.57	10.20–13.00 13.00–15.45	— —	27 27	76 75	NNE NNE	1·3 3·0	As above

DISCUSSION

Area A

SO_2 was detected seven times (0·015–0·8 p.p.m.) and was not detectable eight times (less than 0·002 p.p.m.). Inside the factory the SO_2 concentration varied from 0·156 to 0·800 p.p.m., always giving rise to a strong irritating odour. It was especially severe during working hours owing to the use of open vessels for the nickel extraction process. Modification of the plant design would probably lead to a marked reduction in the level of SO_2 concentration. Irritating odours were experienced downwind of the factory.

TABLE 3. AREA C

Measuring point	Measuring date	Sampling time	SO_2 (p.p.m)	NO_2 (p.p.m)	Weather condition				Remarks
					Temp. (°C)	Humidity (%)	Direction of wind	Velocity of wind (m/sec)	
T	26.8.57	10.00–12.10	0·234	0·481	25	65	E	3·8	Smell of SO_2 and silicofluoride
		12.10–15.10	0·249	0·672	26	65	ENE	4·4	
		15.15–16.00	0·611		26	58	ENE	3·8	
1	27.8.57	11.00–13.30	0·013	—*	24	73	S	3·2	Many factories in the area
		13.30–16.00	0·021	—	24	78	WSW	3·2	
2	28.8.57	10.30–13.10	—	—	26	79	SW	2·2	As above
		13.10–15.40	0·008	—	26	77	SW	2·6	
P	29.8.57	10.45–12.30	0·193	0·219	28	70	ENE	4·4	Perpetual odour of SO_2
		12.30–14.00	0·295		27	75	NE	4·6	
		14.10–15.15	0·230		27	70	NNE	4·2	
3	30.8.57	10.15–12.30	0·014		29	75	S	3·0	Occasional odour of SO_2
		12.30–15.30	0·011	0·259	29	65	SW	1·5	
N_1	2.9.57	10.30–12.00	—	15·445	26	70	N	1·5	Acid SO_2 odour, rather irritating
		12.10–13.35	—	16·406	29	74	NNW	5·2	
		13.50–15.20	—	15·059	29	74	N	5·9	
N_2	3.9.57	10.30–12.00	—	1·149	29	70	NNE	3·0	Smell of SO_2
		12.00–13.30	—	0·584	31	71	NNE	0·7	
		13.30–15.10	0·055	0·320	31	64	N	4·2	
4	4.9.57	10.40–12.10	0·140	—	29	68	NNE	2·8	Sometimes severe SO_2 odour; around this area are homes and houses of the factory workers
		12.15–13.00	0·061		29	68	ENE	2·6	
		13.05–14.30	0·337	—	29	67	,,	4·4	
		14.35–15.20	0·370		29	67	,,	4·6	
		15.25–16.00	0·085	—	29	67	,,	5·0	

* Dashes indicate less than 0·04 p.p.m.

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Area B

Of 14 determinations of SO_2 concentration, only 4 were positive (0·009–0·02 p.p.m.). At measuring point 1, SO_2 concentrations of the order of 0·01 p.p.m. were observed on two occasions. In the factory the concentration of SO_2 was low (0·016–0·020 p.p.m.). Each section of the sulphuric acid plant had been equipped with gas washing equipment of the Venturi scrubber type in October 1956. Since that date there had been a considerable improvement in the atmospheric odour, and in the quality of agricultural products grown in the surrounding district.

Area C

Since there were many factories producing sulphuric acid by the lead chamber process in this area, it was decided to measure concentrations of NO_2 as well as SO_2. Of twenty-three determinations of SO_2 concentration, seventeen were positive (0·008–0·6 p.p.m.). NO_2 was detected ten times (0·20–16·4 p.p.m.) and was undetectable seven times (less than 0·02 p.p.m.).

At factory *T* the SO_2 concentration varied from 0·234 to 0·611 p.p.m., whilst the NO_2 concentration was in the range 0·481–0·672 p.p.m. The process of making chemical fertilizer gave rise to a strong odour of silico-fluoride. The fume-arresting equipment at this factory was inadequate. At factory *P* the SO_2 concentration varied in the range 0·193–0·295 p.p.m. NO_2 was detected once (0·219 p.p.m.). Although no gas-washing equipment was in operation very little odour was detectable. Despite the odour of SO_2 at factory N_2, it was not measurable owing to the high concentrations of NO_2 (0·584–16·406 p.p.m.). Although preventive measures had been taken, they were clearly inadequate.

At observation points 1 and 2 the concentrations of SO_2 and NO_2 were low. Observation points 3 and 4, on the leeward side of the three factories, showed high SO_2 concentrations (0·061–0·370 p.p.m.), and at these points there was a severe irritating odour. The preventive measures taken by the factories in this area were inadequate. Effective gas-washing equipment should be used.

It is now known that SO_2 and NO_2 mutually interfere in the methods of analysis which have been used. It is probable that the failure to detect SO_2 at factory N_2 was due to the prevailing high concentration of NO_2.

Tests were carried out using known mixtures of SO_2 and NO_2. It was assumed that the efficiency of absorption of the SO_2 and NO_2 in the mixture by the absorbing

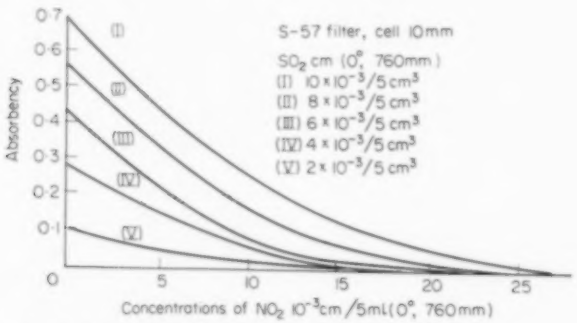

FIG. 4. Influence of NO_2 on absorbency of SO_2 test solutions.

solution was 100 per cent. Fig. 4 shows the influence of NO_2 on the colour development of the fuchsin-formaldehyde reagent. It is seen that the absorbency of the solution decreases with increasing concentrations of NO_2. When the concentration of NO_2 exceeds 20×10^{-3} ml (760 mm, 0° C) per 5ml, SO_2 is undetectable. Fig. 5

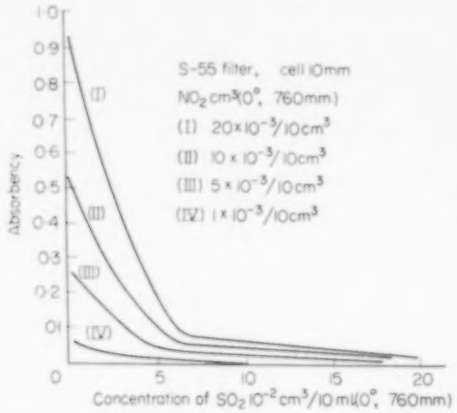

FIG. 5. Influence of SO_2 on absorbency of NO_2 test solutions.

shows the effect of SO_2 on the absorbency of the colour reagent in the test for NO_2. In the presence of SO_2 concentrations in excess of 5×10^{-2} ml/10 ml NO_2 cannot be detected in the range 1×10^{-3}–20×10^{-3} ml/10 ml.

To confirm the above data a 50 l. sample of air containing 0·2 p.p.m. of both NO_2 and SO_2 was passed through the absorbing solution, which should then have contained 10×10^{-3} ml of each, assuming that the absorption efficiency is 100 per cent. From Figs. 4 and 5 it can be seen that the observed concentrations of SO_2 and NO_2 should be 60 per cent and 40 per cent low respectively. As expected, the observed concentrations were 0·08 p.p.m. of SO_2 and 0·12 p.p.m. of NO_2. This explains why SO_2 could not be detected when there were high concentrations of NO_2.

Examination of the mutual interference of SO_2 and NO_2 in the analysis procedures will be continued.

Acknowledgements—The authors wish to express their sincere thanks to Mr. HIROTA and Mr. NOMOTO of the Public Health Division, Health Bureau of Tokyo Metropolitan Office, for their assistance in this investigation. They are also grateful to the factory authorities and residents of the areas which were investigated.

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Int. J. Air Poll. Pergamon Press 1959. Vol. 2, pp. 84–86. Printed in Great Britain

ATMOSPHERIC POLLUTION IN GREAT BRITAIN
THE LONDON FOG OF 2–5 DECEMBER, 1957

A. E. MARTIN
Ministry of Health
(*Received* 29 *April* 1959)

Abstract—The London fog of 2–5 December, 1957 was accompanied by a marked increase in atmospheric pollution and an immediate rise in mortality and in the demand for hospital beds. Deaths due to the fog in Greater London are estimated to number at least 763 and may have been 1000. Comparisons are made with other London fogs and the possible effects on mortality of fogs of shorter duration is discussed.

IN addition to the fog disaster of 5–8 December, 1952, fogs associated with a high level of atmospheric pollution and with appreciable increases in the numbers of deaths have occurred in Greater London from 26 November to 1 December 1948, from 3 January to 6 January 1956, and from 2 to 5 December 1957. The latter is reviewed in the Annual Report of the Chief Medical Officer of the Ministry of Health and has been described in detail by BRADLEY *et al.* (1958) and SCOTT (1958).

ATMOSPHERIC CONDITIONS

The 36 hr preceding the onset of the 1957 fog were somewhat unusual. An anticyclone was centred over Western Europe and at Kew Observatory both 1 and 2 December were clear and cloudless with a low humidity which prevented fog formation. A smoke haze was present and atmospheric pollution was doubled. Moist air reached London in the late afternoon of 2 December and with a fall in temperature fog developed. This persisted for 3 days, clearing rapidly in all parts of London towards midnight of 5 December. A feature of the fog was that during much of the time light winds of from 1 to 5 knots prevailed and the fog, although very dense in places, was variable, temporary remissions with visibilities of from 100 to 500 yd occurring in some areas. Remissions such as these were absent during the great fog of December 1952 when during most of the time a dead calm prevailed.

Atmospheric pollution readings both of black suspended matter and of SO_2 showed a gradual and constant rise during the 3 days, reaching a maximum on 5 December. In the central and western parts of London, the atmospheric pollution, although raised to a serious level was considerably below that in 1952. On the eastern fringe of London high values were recorded and at Woolwich and Hornchurch the figures were above the corresponding ones for 1952. At Woolwich in particular concentrations of black suspended matter of 5·43 and 5·22 mg/m^3 and sulphur dioxide concentrations of 0·95 and 0·93 p.p.m. on 4 and 5 December respectively are comparable in amounts to the maximum concentrations recorded in Central London in 1952.

MORTALITY AND MORBIDITY

For Greater London, a special tabulation of deaths related to the day of occurrence was prepared by the General Register Office. This showed that the total number of

deaths from all causes rose from a level of from 240 to 280 a day before the fog to 350 on 3 December, 392 on 4 December (excluding 87 deaths in the Lewisham train disaster, an indirect result of the fog) to 472 on 5 December. Mortality was heaviest on the eastern side of the city. No cause other than fog can be found for the increase in mortality; the epidemic of Asian influenza which had occurred during September and October was over and few deaths during the fog period were certified as being due to influenza.

Estimation of the numbers of deaths attributable to a fog is hazardous as much depends on the curve which it is assumed mortality would have followed had there been no fog. BRADLEY *et al.* (1958) estimate that the deaths resulting from the 1957

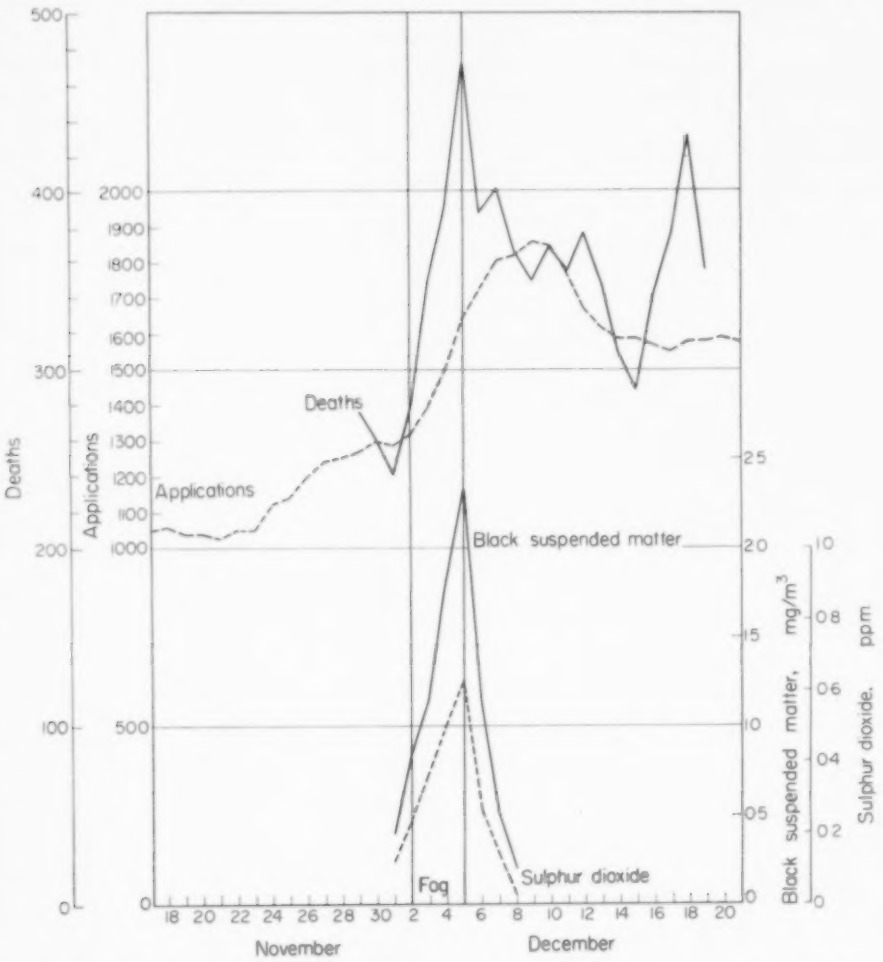

FIG. 1. Deaths in Greater London classified according to the day of occurrence together with 7-day moving totals of applications for admission to hospital made to the Emergency Bed Service Bureau and mean daily atmospheric pollution figures. (Deaths in the Lewisham train disaster are excluded.)

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fog numbered at least 763 and may have been over 1000. This compares with estimates of roughly 1000 for the January 1956 fog, 4000 for the fog of December 1952 and 700–800 for that of November/December 1948.

No estimate of the morbidity resulting from the fog is possible, but the daily numbers of applications to the London Emergency Bed Service Bureau provides a sensitive index of the trend of sickness in the area and gives a clear indication that the morbidity curve resulting from the fog was similar to that for mortality.

LOGAN (1956) contrasted the mortality associated with fogs during recent years with the apparent absence of any increased mortality in many of the earlier incidents, and suggested that this might indicate either that London fogs have recently become more toxic or that there has been an increase in the proportion of the population vulnerable to their effects. In his report for 1957 the Chief Medical Officer has pointed out that an important feature of the recent fogs has been that mortality has begun to rise on the first day of the fog at a time before the atmospheric pollution has reached its maximum, and that this suggests that many fogs of shorter duration may be associated with a definite mortality which, though serious, may not be sufficiently large to be obvious in the mortality statistics. In an investigation of London fogs during the years 1954–56 (LONDON COUNTY COUNCIL, 1957; GORE and SHADDICK, 1958) it has already been suggested that in London there is a critical level of four times the customary winter average of atmospheric pollution above which a fog will cause a marked immediate excess mortality. The importance of such observations is evident, and further studies will have to be made of the effect on this critical level of the duration of fogs and of variations in the constituents of the pollution. Thus during the winter of 1958–59 there have been a number of fogs, some of short duration though of high density. Their effect on health has yet to be assessed, but in one, in Salford, the smoke and sulphur dioxide content for a short time exceeded that of the London fog of 1952 (BURN, 1959). SCOTT (1958) has pointed out that the fog of December 1957 had a higher SO_2 and lower smoke content than that of January 1956. Changes such as this will require careful observation and much research in the future for problems associated with gaseous pollutants of the atmosphere, particularly sulphur dioxide, have yet to be solved. This, as the Chief Medical Officer points out in his review, will tax the resources of all engaged in the Clean Air campaign.

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SMOGS IN BRITAIN AND THE ASSOCIATED WEATHER

P. J. MEADE
Meteorological Office, London
(*Received* 1 *May* 1959)

Abstract—The smog conditions of the 1958–59 winter in Great Britain are discussed and their necessary association with quiet, anticyclonic conditions is emphasized. The argument is illustrated by reference to some of the worst smog incidents which occurred in January and February. The possibility is mentioned of instituting a form of meteorological control with the object of reducing the output of smoke at times when the weather conditions are favourable for the formation of persistent fog.

A LARGE number of people in Great Britain will remember the winter of 1958–59 mainly for its association with smog. Those who suffered most may have memories of little else, and even the healthiest of the inhabitants of certain large towns would probably be prepared to agree that on occasion they were more painfully aware of smog during the past winter than ever before.

The worst conditions of smog occurred during January and February, and it is not merely a coincidence that quiet, anticyclonic conditions were a prominent feature of the weather during those two months. In winter the large central area of an anticyclone, with very light winds or calms and probably a subsidence inversion aloft, provides the most favourable situation possible for the formation of fog and for the retention within a shallow surface layer of the smoke discharged from chimneys. Winter is the important season because then the heat from the sun may not be strong enough to disperse the fog with its embedded impurities, and thus a clearance may have to wait until freshening winds arrive when at last the anticyclone moves away. Moreover, while the smog persists, the temperature of the air falls, inevitably the consumption of fuel rises, so the smog intensifies—and so on.

In order to appreciate more precisely the association of smog with a certain weather type, let us select for examination some of the worst incidents of last January and February.

The first example is the 4-day period from 13 to 16 January. On 13 January fog and frost occurred in Lancashire and persisted until the following day, by which time many parts of northeast, central and eastern England were similarly affected. At this time the area of fog was shifting somewhat and, although no improvement occurred in many parts of the Midlands and East Anglia, there were clearances in Lancashire, but the Glasgow area became foggy with temperatures below freezing point. During these 4 days the British Isles were under the influence first of an anticyclone extending from near Greenland and then of another high pressure system to the south. The pressure distribution over the British Isles at 0900 hours on 15 January, 1959, is given in Fig. 1, where the areas from which fog was reported at about this time are indicated by shading. As shown in the figure, the main anticyclonic centre was away to the northwest but an area of calm or light winds covered the whole of Scotland and the greater part of England. The shifting of the fog area during the 4-day period reflected the slight changes as between areas of very light winds and areas of rather stronger winds over a large expanse of quiet weather.

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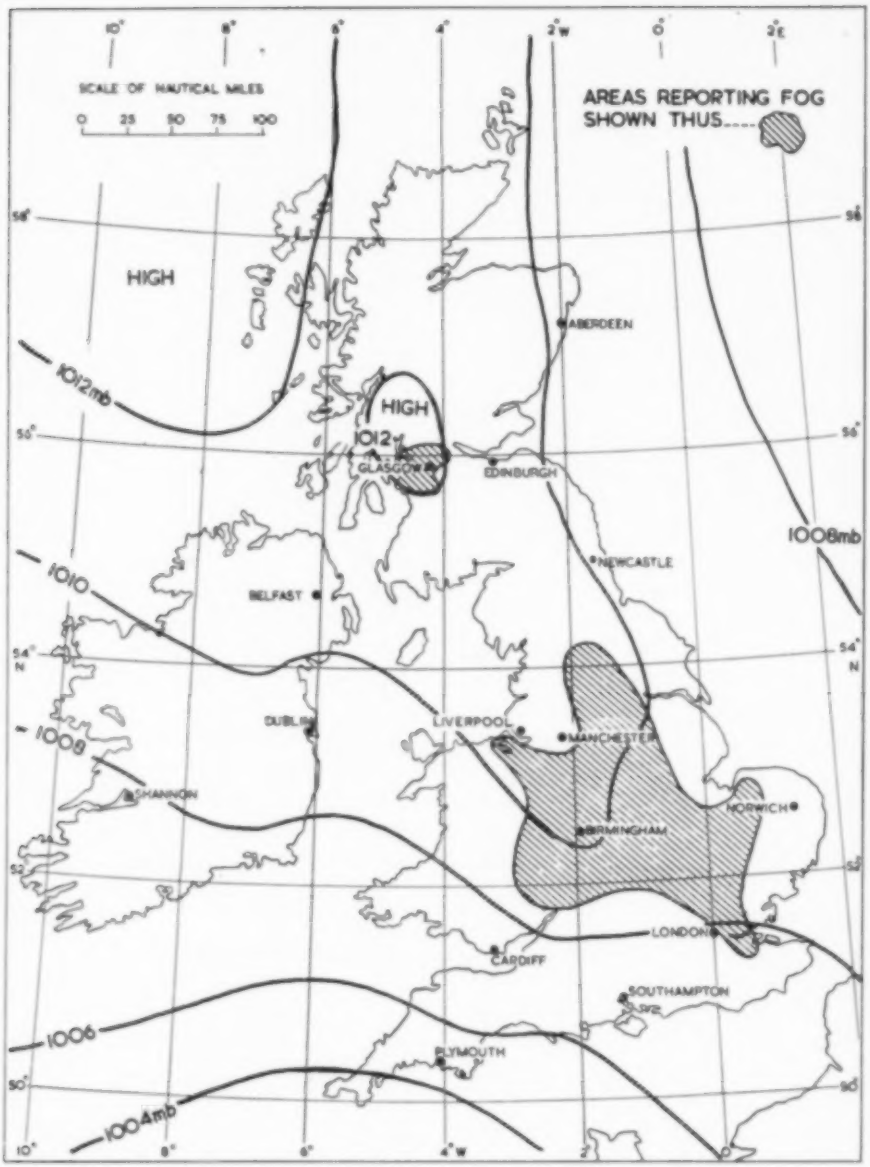

FIG. 1. Pressure distribution and fog areas at 0900 hours 15 January, 1959.

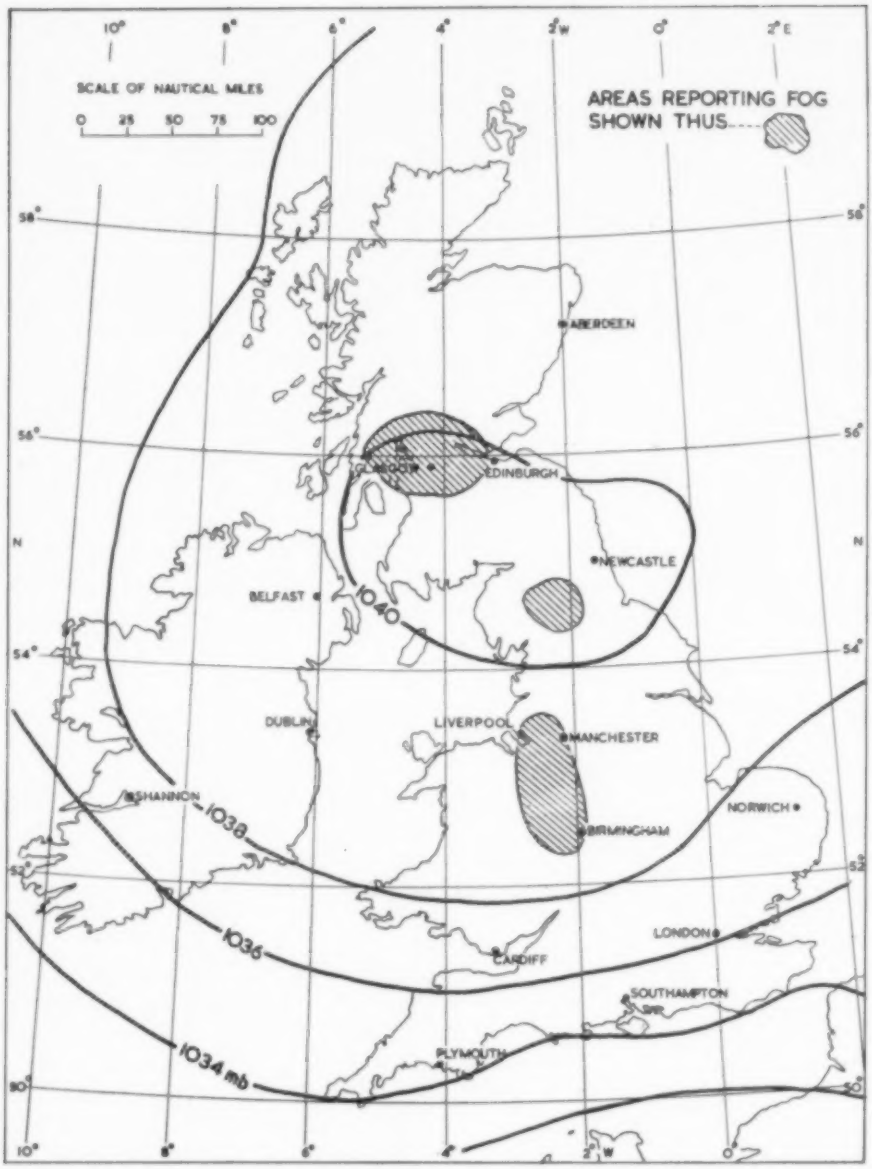

FIG. 2. Pressure distribution and fog areas at 0900 hours 2 February, 1959.

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Another bad period of smog was experienced in Great Britain during the final days of January and then, after a brief respite over the whole country, there was a return of foggy conditions to many places where the first week of February became notable for smog of unusual severity.

On 23 January, there was dense fog in the Mersey area and in Lancashire. By the following day these conditions had become widespread over much of England and Scotland. In the Forth–Clyde valley fog persisted for 2 days and in other areas the clearances were short-lived with temperatures constantly below the freezing point in many places. During this period the weather over the British Isles was again dominated by a large anticyclone the centre of which moved slowly from the North Sea to Germany without, however, giving rise to any moderate or strong pressure gradients over Britain.

The foggy air was displaced on 30 January by the southward movement of a cold front, but already another anticyclone was approaching the British Isles from the west and was to be the dominant factor in the weather for the next 8 or 9 days. During the first 3 days of February this anticyclone was centred over Scotland, as shown in Fig. 2, and during that period the Forth–Clyde valley was enveloped in smog. Then as the centre of the anticyclone moved, first to the east and then to the south, Britain was free from fog for a whole day, but it reappeared on 5 February, this time in the southern and central parts of England. For the next few days the fog became more widespread and in many parts all forms of transport were halted for a time. On 8 February, the fog largely cleared but southern England was to experience widespread but non-persistent fog several more times before the month ended.

SMOG'S ESSENTIAL ALLY—THE ANTICYCLONE

After this review of the January and February smogs it may be superfluous further to labour the point that quiet, anticyclonic conditions are an indispensable accompaniment of the more serious smogs. However, there are some aspects that are worth emphasizing and indeed must be continually stressed so long as smogs remain with us.

With our present methods of fuel consumption, it needs only a suitable weather situation in winter for there to be a serious risk of smog. A constant factor is the smoke itself which is being discharged to the atmosphere throughout the winter from chimneys all over the country. The variable factor is the weather. From one year to another there are variations, perhaps small ones, in the positions of anticyclones, but these variations are sufficient in themselves to explain why the worst smog hits Glasgow one year, Manchester another and possibly London the third year. The weather factor is not only variable, it is also the one factor that can justifiably be regarded as beyond human control. The notorious London smog of December 1952 tasted for only 4 days but it was blamed for the deaths of more than 4000 people. The weather situation then was, for the London area, unusual in its persistence, but no-one can say it will not recur in 1, 5 or 10 yr time.

METEOROLOGICAL CONTROL

The foregoing discussion brings to mind a course of action that has been taken elsewhere. Accepting our inability to control the weather and assuming that the output of smoke may not be reduced substantially for some time, would it be possible

to reduce the smoke emission on the few occasions that the weather makes it important to do so? This seems a very practical way of considering the problem, because there are many days when it matters not at all whether domestic and other chimneys emit smoke. On the other hand, for any one district in Great Britain there are a few days each year when smoke may be trapped for many hours in a shallow surface layer and cause smog. Obviously on these days it would be highly beneficial if little or no smoke were emitted. This would involve a system of meteorological control similar to the measures which have been introduced in parts of Canada and the United States for reducing the output of pollutants by heavy industry at times when the weather conditions are unfavourable for rapid dispersion. A solution of this nature would raise many practical difficulties and would demand great flexibility on the part of industry, but it might provide a useful intermediate step pending a vast increase in the number of smokeless zones.

Acknowledgement—This paper is published by permission of the Director General of the Meteorological Office.

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Int. J. Air Poll. Pergamon Press 1959. Vol. 2, pp. 92–108. Printed in Great Britain

Review Articles

THE PROBLEM OF ATMOSPHERIC DIFFUSION

E. L. DEACON
C.S.I.R.O. Division of Meteorological Physics, Aspendale, Victoria, Australia
(*Received* 9 *March* 1959)

Abstract—A general account is given of some of the main lines of attack on the problem of atmospheric diffusion and of the difficulties encountered.

The important role of atmospheric stability in relation to turbulence and diffusion is illustrated and discussed.

THE disposal of unpleasant and harmful waste products into the atmosphere has long been agreed to need regulation. Indeed as early as 1273 the English Parliament passed an Act prohibiting the burning of coal in London. Unfortunately this gallant attempt to nip an evil in the bud met with singularly little long-term success. But it is still very true that atmospheric pollution is a disease of industrial communities for which prevention is better than cure. When suffering from the disease, however, we are more likely to obtain some relief if all its aspects are well understood, and one of these, and an important one, is the role of atmospheric turbulence in dispersing pollution.

The intention of this article is to give some idea of the lines along which the study of atmospheric diffusion has been progressing while avoiding as far as possible the more abstruse aspects which may be followed up with the aid of an excellent recent review, complete with many references, viz. " Turbulent diffusion in the atmosphere " by PRIESTLEY *et al.* (1958).

Having been given the directive that an account in philosophical vein would be most acceptable, the author experienced a period of alarm and despondency until, chancing upon a remark of Bertrand Russell that " Science is what you know, philosophy is what you don't know ", his courage returned with the reflection that the chosen subject might, after all, lend itself particularly well to the desired treatment.

THE ANALOGY WITH MOLECULAR DIFFUSION AND ITS FAILURE

The diffusion of matter by molecular agitation is analogous to the conduction of heat in isotropic media as was recognized by FICK in 1955. The Fickian treatment of diffusion therefore rests on the simple proportionality between the flux F of diffusing substance in a given direction x and the concentration gradient $(\partial c/\partial x)$ in that direction. In this equation, viz.

$$F = -D\,\partial c/\partial x$$

D, the molecular diffusivity, is analogous to the thermal conductivity in the heat diffusion case. For a given combination of medium and diffusing substance D is a constant at any particular temperature and many problems of molecular diffusion are therefore susceptible to relatively simple solution.

The rate of diffusion in the atmosphere is, of course, nearly always vastly greater than could be produced by molecular activity alone. Observation shows that a

small smoke puff released in the atmosphere often grows to a diameter of the order of 100m in 5 min, whereas by molecular diffusion alone the diameter after this time would be less than $\frac{1}{2}$m. This rapid dispersion is the result of the chaotic swirling and intermingling of masses of fluid on a very much greater scale than that of the molecular mean free path.

Nevertheless it was natural that early studies of atmospheric turbulent diffusion by such pioneers of turbulence theory as G. I. TAYLOR, L. F. RICHARDSON and W. SCHMIDT should have been directed in the first place to seeing how far the Fickian treatment could give a useful description of the phenomena and some indication of the magnitude of the turbulent diffusion coefficient K analogous to D in the above equation. TAYLOR found, for example, that the distribution of wind velocity in the lowest 1000m or so of the atmosphere—the friction layer—could broadly be explained by values of K (for momentum transfer in this instance) of the order of 10^3 to 10^5 cm^2/sec; values greater than the molecular value by a factor from 10^4 to 10^6.

It was recognized as unlikely, to say the least, that a constant universal value of K would be found suitable in treating all the various manifestations of atmospheric diffusion. A very wide range of K values did indeed soon appear in the meteorological literature and the complexity of the subject began to be apparent.

Following the inception by JOHNSON in 1921 of systematic quantitative studies of the diffusion of smoke and gas, mainly from sources on the ground, it was soon found that as between different occasions the values of K varied widely with such factors as wind speed, atmospheric stability (i.e. vertical temperature gradient) and the nature of the underlying surface as regards roughness.

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An approximate proportionality of transfer coefficient to wind speed was not surprising, but the great influence of the vertical temperature gradient was an interesting and obviously more complex phenomenon. It is actually the vertical density gradient that is physically important, but for air the simple inverse relationship between absolute temperature and density makes it more convenient to work in terms of temperature gradient.

By day the warming of the ground by solar radiation causes the superincumbent air layers to become warmer and therefore lighter than those above, so that vigorous convective up currents with broader compensating down currents give a brisk churning action which greatly increases the diffusive power of the atmosphere. These conditions are referred to as unstable or strong lapse conditions and typically there is a marked decrease of temperature with height up to 50–100m.

By night, particularly with a clear sky, the ground loses heat by radiation to space and sets up a surface temperature inversion, i.e. temperature increasing upwards to heights of the order of 100m. The stable density gradient largely damps out turbulence, and in extreme cases the flow becomes virtually streamlined. These conditions are referred to in the following as stable conditions and the state of no appreciable density stratification effects is called neutral stability.*

The striking difference in turbulence conditions between unstable and stable conditions is illustrated in Fig. 1, which shows recordings of the vertical component of

* Because of the decrease of pressure with height neutral stability occurs when temperature decreases with height at the rate of 1° C per 100m—the dry adiabatic lapse rate as it is called. A " pocket " of air descending 100m under these conditions would be warmed 1° C by compression and so still be at the same density as the surrounding air on its arrival at the lower level.

eddy velocity made at 29m above open grassland, the mean wind speed being almost exactly the same in the two cases (4·5 m/sec). The vastly different behaviour of smoke from bonfires as between two such occasions is a matter of common observation.

Had it proved only to be necessary to cope with variations of the diffusion coefficient K with different prevailing meteorological conditions the problem would have

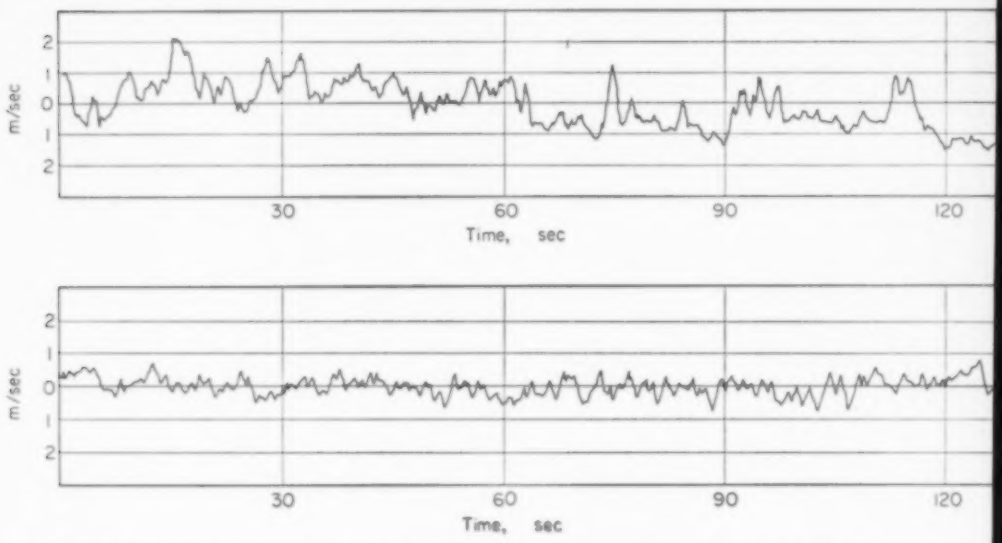

FIG. 1. Specimen recordings of vertical eddy velocity at 29m above grassland at Edithvale, Victoria: the upper record is for a clear summer day (local time 1400hr) and the lower for a cloudless early evening of the same day.

been one of relative simplicity. But the observational work soon showed that there were other more baffling complexities. Diffusion in the vertical was found to display markedly different characteristics from that affecting the horizontal spread of diffusing matter. The vertical diffusivity K_z was found to increase rapidly with height, whereas the generally larger cross-wind horizontal component K_y exhibited less variation.

But the most intractable and discomforting finding was one which constitutes a fundamental objection to the use of the K concept: it became clear that even with specified meteorological conditions and a given site no unique values of K_y, K_z, etc., could be assigned to any point in the field of flow but that K varied with the scale of diffusion being considered. The nature of this difficulty may be illustrated by considering imaginary fields of turbulence with simple structure. First, the fluid is supposed to contain only a fine-grained turbulence characterized by circular whirls of say 1 cm diameter. This state would correspond to a medium of constant K, and the separation of a cluster of particles originally very close together would be expected to follow the law deduced by Einstein for Brownian movement, namely

$$\sigma = \sqrt{(2Kt)}$$

where σ is the standard deviation of the distance of the particles from the centre of

the puff after time t. After a rapid initial dispersion the cluster would grow more and more slowly.

Now let us suppose this fluid to contain additionally another turbulence on a very much greater scale, 1m for example. Then a cluster of particles from a point source would for some time diffuse under the action of the small-scale turbulence alone, because over small separations the velocity gradients in the fluid would be almost entirely those associated with the fine-grained turbulence. The path of the growing puff would, of course, be more or less sinuous owing to the effect of the large eddies but that at first would be their one effect. When, however, the cluster had grown to be comparable in size with that of the large eddies the diffusing effect of these would soon predominate and the smoke puff would expand very rapidly while of size similar to these eddies. After that the scatter would tend to become once more proportional to the square root of the elapsed time.

The history of our smoke puff (or the trail from a continuous point source which is similar) is illustrated diagrammatically in Fig. 2 in which the general drift of fluid

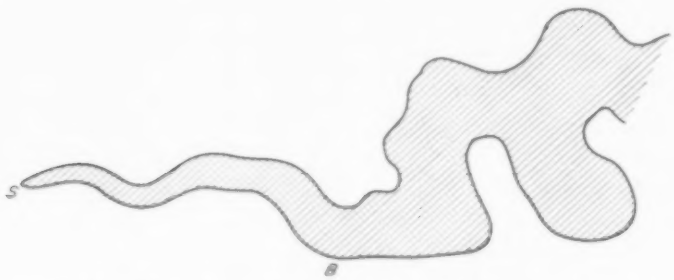

FIG. 2. The expected behaviour of a smoke trail in a turbulent flow containing two very different scales of eddy motion.

is from left to right. The diffusion (as distinct from meandering) of the smoke from source S as far as B could be described by a K value appropriate to the fine-grained turbulence. Beyond B we would soon need to use a much larger K associated with the large eddies.

The natural wind contains eddies covering a great range of sizes, as is evident from the turbulent velocity fluctuations shown in Fig. 1. There is, of course, in such records an inverse proportionality between eddy size and the frequency of oscillation: eddy size and frequency are to some extent analogous to wavelength and frequency when we are dealing with light and sound. Corresponding to spectra of light and of noise, we may speak of the spectrum of turbulence, i.e. the distribution of eddy kinetic energy over the frequency range in whatever field of steady state turbulent motion we may be studying.

A physically adequate treatment of turbulent diffusion needs formulation in terms of the spectrum of turbulence as was first fully realized following a classical contribution by TAYLOR in 1920 which has given rise to the statistical theory of turbulence as well as to significant advances in other fields (e.g. communications engineering) much concerned with quantities fluctuating with time in the manner illustrated by the eddy velocities in Fig. 1.

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THE STATISTICAL THEORY OF TURBULENCE

The peregrinations of particles emitted, for example, by a point source will be describable in statistical terms if we know how the particle velocity at one moment is correlated with that at later times. If, at one extreme, the correlation coefficient is always unity then the particles travel in straight paths at uniform speed and so scatter like shot from a gun. In this case the r.m.s. value of the particle displacements σ from the centre of the cloud increases proportionally with elapsed time t. At the other extreme a total lack of correlation between the motions at all time intervals greater than some small value would correspond to a diffusion of the molecular type for which

$$\sigma \propto \sqrt{t}.$$

In the general case of a homogeneous field of turbulence TAYLOR showed that

$$\sigma^2 = 2\tilde{u}^2 \int_0^T \int_0^t R(\xi)\, d\xi\, dt \tag{1}$$

where $\tilde{u}$ = r.m.s. eddy velocity
$R(\xi)$ = the correlation coefficient between the velocities affecting the particles at one instant and those at ξ sec later
T = elapsed time from release of particles.

For diffusion in any specific direction, σ, $\tilde{u}$ and $R(\xi)$ all refer to components in that direction.

The graph of $R(\xi)$ against time is called the auto-correlation curve or auto-correlogram. On general physical grounds it is evident that there should be a relation between the auto-correlation curve and the spectrum. For large eddies $R(\xi)$ will fall to zero more slowly than when the eddies are small. An auto-correlation curve showing a slow decay indicates therefore a spectrum containing a large proportion of low frequencies or vice versa. TAYLOR showed how the spectrum curve could be derived mathematically from the auto-correlation curve, although the calculation is a rather laborious one.

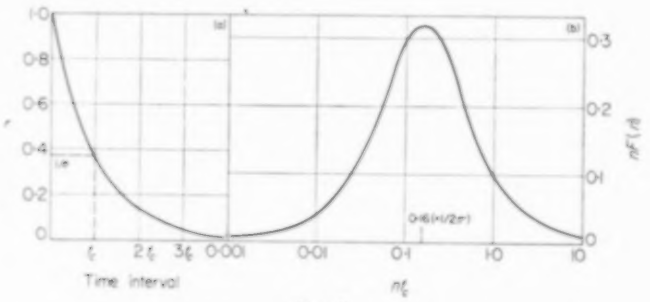

FIG. 3.
(a) Exponential auto-correlation curve with a time constant of the decay $= t_e$.
(b) The corresponding spectrum curve where n = frequency.

An example of the correspondence between auto-correlation curve and spectrum is given in Fig. 3 for a simple case which is nevertheless useful because observed auto-correlations in the present context often approximate roughly to this form. It will be supposed that particle velocities in some given direction give an $R(\xi)$ decreasing

exponentially with time as in Fig. 3a. The corresponding spectrum is shown in Fig. 3b, with frequency plotted on a logarithmic scale as is most convenient for turbulence spectra owing to the wide range of frequencies involved. Then $nF(n)$ has the significance that the fraction of $\tilde{u}^2$ (total mean square velocity fluctuation or turbulent energy per unit mass of air) associated with a band of frequencies, say from n_1 to n_2, is represented by the area under the curve between the ordinates at n_1 and n_2.

Unfortunately for the study of atmospheric diffusion the $R(\xi)$ line of attack is proving very difficult to exploit in a really satisfactory manner for several reasons which will appear in the sequel.

The first difficulty arises from the very nature of turbulent diffusion which demands a treatment in terms of the erratic progress of fluid particles through the field of flow; in other words, some form of Lagrangian description of turbulent structure. This requirement is hard for the experimentalist to meet; to secure the requisite information in sufficient quantity for satisfactory statistical treatment is a very laborious undertaking and one not susceptible to automation of the kind now increasingly employed to secure some types of observational material on a statistical basis.

Work has been done using suitable markers carried by the wind: zero-lift balloons, soap bubbles, dandelion seeds and smoke puffs have all been used at various times according to the scale of atmospheric turbulence under study. With most of the existing techniques it is difficult to follow the tracers for sufficiently great distances. This and the amount of labour involved has so far prevented a large enough body of data being amassed to be of much real assistance to the theoretician.

Observing the structure of turbulence with a fixed installation is in comparison relatively simple and a mounting body of knowledge is resulting from such studies. It is hoped that this may be capable of translation into Lagrangian terms, but whether this is possible with sufficient accuracy or, indeed, what is sufficient accuracy, are questions currently being followed up in several quarters, as was evident from the attention given to this matter at the International Symposium on Atmospheric Diffusion and Air Pollution held at Oxford in August 1958 (SCORER, 1958).

An example of the first simultaneous determinations of atmospheric turbulence spectra by the two methods is shown in Fig. 4. The Lagrangian spectrum was from observations on zero-lift balloons released from the 91m stage on a lattice tower which carried at the same level the instruments for the fixed point spectra. A typical difference in the predominant frequencies is evident; the Lagrangian frequencies are lower by a factor of around 4. One reason for the higher frequencies with the fixed instruments is an effect of the eddy pattern in the air being swept over the tower by the wind; a given spatial pattern would give rise to higher frequencies the stronger the wind. But there are quite probably other factors involved—it is too soon to say.

One way of deriving some information about the behaviour of $R(\xi)$ is to utilize equation 1 in conjunction with measurements of σ and $\tilde{u}$. HAY and PASQUILL (1957) have recently exploited this device of working backwards from diffusion data to a knowledge of $R(\xi)$ by observing values of $\tilde{u}$ and the vertical spread of material at distances from 100 to 500m downwind of a source carried at a height of 150m on a balloon cable. From 10 emissions made over Salisbury Plain under neutral conditions, they found

$$\sigma \sim \tilde{u}T,$$

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which one obtains from equation 1 for values of T such that $R(\xi)$ has not fallen much below unity in the interval 0 to T. In these experiments T had values up to 70 sec, whereas the auto-correlation curve from the fixed point measurements showed a decay to zero in about 15 sec. This again shows that the Lagrangian spectral

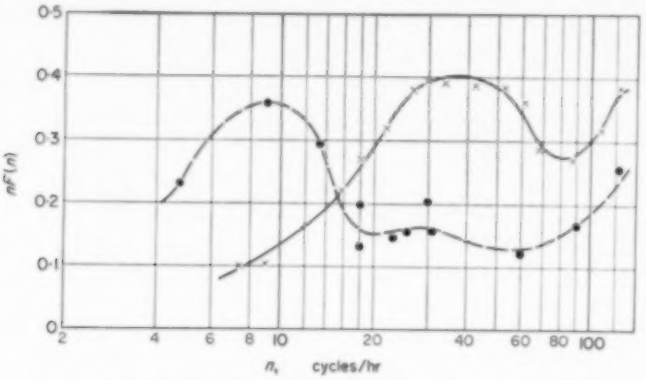

FIG. 4. Spectra of vertical eddy energy from recordings at 91m on a tower (full line) and from the simultaneous movements of a zero-lift balloon released from the same height (broken line). (After F. GIFFORD (1955).)

frequencies important for diffusion are generally much lower than those indicated by a stationary recording instrument. In further work on ground sources HAY and PASQUILL (1959) have found about a four-fold ratio in the same sense.

Turning now to some results of the studies with fixed installations, Fig. 1 shows typical records of the vertical eddy velocity fluctuations measured at 29m using a tower standing in level meadowland and from the complete recordings (only shown in part in Fig. 1) the corresponding auto-correlation curves and eddy spectra are given in Fig. 5. The wind speeds were identical on these two occasions (4·5m/sec), and the striking differences between the auto-correlations and the spectra are due to the differing stability in the surface atmospheric layers as between a clear summer daytime and the early evening. The spectrum curves are drawn so that the area under the curve between two ordinates is proportional to the eddy energy associated with that frequency band and the two spectra are related in the same manner. The total eddying energy (vertical component) is rather more than four times greater for the unstable occasion than for the evening run, and much of the energy by day is associated with low frequency fluctuations which are absent or very small by night. The several peaks in the daytime spectrum at frequencies above 1 cycle/min are mainly due to the limited sample of turbulence analysed: the mean of several spectra taken under similar conditions would show a smoother distribution with only one maximum in this region. However, there is evidence to show that the low frequency peak (at ~0·8 cycle/min) is associated with the passage over the tower of a pattern of convection currents favoured by the strong heating of the ground and the moderately light wind.

It has long been known that the horizontal components of turbulence near the earth's surface are more energetic than the vertical component; the ground exerts a restraint on vertical motion which is very marked at low heights. Fig. 6 is interesting

as showing that the turbulence at a height as great as 109m also displays a very marked difference between horizontal and vertical motion with a greater proportion of energy associated with low frequency oscillations in the former. The spectrum of vertical motion is found to vary more with changing atmospheric stability conditions

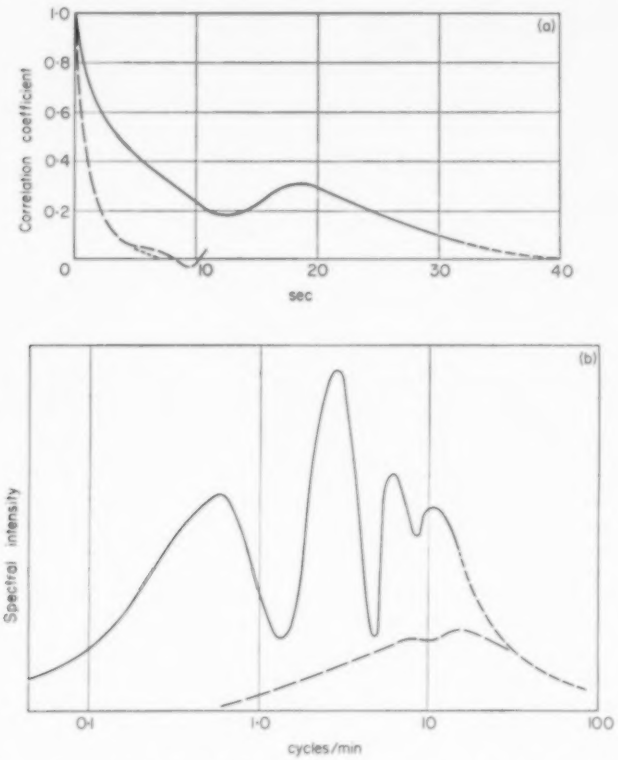

FIG. 5. (a) Auto-correlation curves and (b) corresponding spectra for the vertical eddy velocity recordings shown (in part) in Fig. 1. Unstable conditions—full curves; moderately stable conditions—broken lines. Wind speed 4·5 m/sec at 30 m in each case. (After E. K. WEBB (1955).)

than does the horizontal spectrum. This is, of course, understandable in view of the fact that convective motions arising from an unstable density gradient are likely to have more direct influence on vertical motion than horizontal.

A second difficulty in the application of statistical theory to atmospheric diffusion is connected with the fact that on most occasions the turbulent energy does not fall off at lower frequencies as rapidly as in the simple spectrum of Fig. 3 but extends far into the low frequency region as is well illustrated by Fig. 6. This is most marked with the horizontal motions which affect the lateral diffusion of airborne material. This difficulty has long been recognized—L. F. RICHARDSON drew attention to it—and it arises from the rather artificial separation of atmospheric flow into two parts, the mean flow and the turbulence which is considered to be superimposed upon it. When fluid flow is guided as in pipes and channels, the consideration of turbulent cross-currents is a valid one. When further the flow is taking place under a constant

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driving force or one varying quite slowly in a regular manner, then the full classical Reynolds conception of mean flow and turbulent components can be applied without ambiguity. But apart from a constraint by the ground on motions perpendicular to it, the flow over the earth's surface is seldom steady in this sense and the conceptions

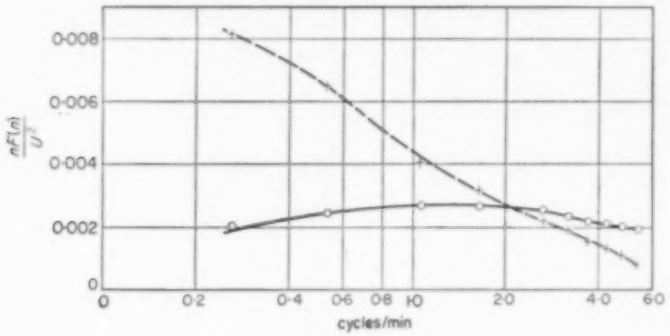

FIG. 6. Spectra of vertical (full line) and horizontal (broken line) components of eddy velocity at a height of 91 m. Each spectrum is the mean of 6, all for moderately unstable conditions and wind speed 7 to 10 m/sec, mean 8·0 m/sec. (After H. A. PANOFSKY and R. A. MCCORMICK (1954).)

of mean flow and eddy fluctuations become correspondingly vague. For this reason diffusion in the horizontal plane will always be less susceptible to precise treatment than vertical diffusion.

A third major complexity of atmospheric turbulence in the frictional boundary layer is the rapid variation in the structure of turbulence with height. This is particularly marked for the vertical eddy motion, the scale of which is found to increase in rough proportionality with height up to 100m or so—i.e. the eddy frequencies of greatest energy at 100m are lower than at 10m by about one order of magnitude and lower than those at 1m by two orders. In the same layer there is also an appreciable variation of mean wind speed and direction with height which is often quite striking at night (stable conditions of stratification). Such shearing motions cause bodily distortions of diffusing clouds of material and can interact in a complex way with the purely turbulent diffusion.

The statistical treatment of turbulence and diffusion has advanced rather more rapidly with the relatively simple fields of turbulence which can be produced in wind tunnels, and in recent years some progress has also been made in the study of turbulent boundary layer flow as a result of a close collaboration between theoreticians and experimentalists. Such laboratory studies have been and will continue to be of great assistance to the worker on atmospheric problems. The controlled and reproducible conditions of the laboratory are favourable to more rapid progress than is possible in the open air. However, there are some limitations to work on the small scale when it comes to transposing the results to a much larger scale. In aeronautical problems this has led to larger and larger wind-tunnels, so that now one of the largest (operated only at night) takes as much electric power as the city of San Francisco. As the turbulence researcher has to make do with more modest equipment, it follows that observational work in the open air must continue to be a vital activity.

The laboratory work, as well as some less extensive investigations in the atmosphere, has given considerable support to some ideas put forward by KOLMOGOROFF in 1941. As a result of these a useful degree of similarity is being found between the smaller scales of turbulence present in many different types of turbulent flow, particularly in those cases where the spectral range is large. The key idea was that smaller eddies are generated by and receive their energy from larger ones. The large scale motion may be very anisotropic as in the atmosphere near the ground, but this anisotropy is progressively lost as energy passes down the scale and is degraded to increasingly random motion ending up as molecular agitation, i.e. heat.

The main differences between turbulent flows produced in a variety of ways reside therefore in the mean flow patterns and grosser features of the turbulence; the finer structure is simpler and of much more universal character and is found to depend on only two factors, the kinematical viscosity of the fluid (i.e. viscosity/density) and the average rate at which turbulent energy is being degraded to heat. Indeed a part of the eddy spectrum should depend only on the last-mentioned factor, the dissipation.

This partial unification of turbulence theory to cover the finer structure of many different fields of turbulent flow is unfortunately not very helpful with most problems of interest in the atmospheric pollution context where diffusion is usually strongly dependent on the coarser properties of the turbulence not embraced by KOLMOGOROFF's similarity theory.

An exception to this may, to some extent, occur when considering such problems as the lateral (cross-wind) spread of a smoke plume. The eddy motion in the horizontal plane is, as we have already seen, not restricted by the ground as are the vertical motions and so, at any given stage in the diffusion of the smoke, there is generally plenty of eddy motion on much larger scales than that most effective in diffusion. This relatively small-scale turbulence may therefore be in the " Kolmogoroff range " to which similarity theory applies and, if so, it can be shown that the lateral diffusion coefficient K should vary as

$$K \propto \epsilon^{1/3} l^{4/3},$$

where ϵ is the rate of viscous dissipation per unit mass of fluid and l is the scale of the diffusion which in this case can be taken to be of the order of the width of the smoke plume. This recalls a result of RICHARDSON (1926) who studied the variation of K with scale over a range of more than 1000: 1. He put together the results from small-scale experiments, from the scatter of balloons over distances of the order of 100 miles and the scatter of volcanic ash over even greater distances. He obtained the then rather mysterious relationship that approximately

$$K = 0{\cdot}2\, l^{4/3},$$

the value of the constant being in c.g.s. units; but it now appears that the similarity theory can largely explain his result.

Diffusion over large distances in the atmosphere is, however, often complicated by factors ignored in a simple treatment such as that above. Convection on the scale of cumulus clouds can feed energy into the turbulence at an intermediate point in the spectrum and so invalidate the Kolmogoroff approach. Marked variations in wind direction and velocity with height and convergence or divergence of the streamlines of the mean flow, as well as frontal phenomena, can grossly distort a cloud of diffus-

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ing material. It was a combination of such effects which caused the remarkable behaviour of the radioactive cloud formed as a result of the accident to a nuclear reactor at Windscale in October 1957. The cloud had spread to 150 km in width by the time it was only 120 km south of Windscale—a rate of spread greatly in excess of what would normally be expected.

In taking stock of the present position in turbulence research it is true to say that progress in building a reasonably rigid logical framework has been rather slow and, particularly with diffusion problems, it will be necessary for some time to come to make do with rather more rickety and less elegant structures arrived at by a combination of *sufficient observational material* with various more or less crude mathematical models. This is not such an unhappy situation as might be imagined. Had it not been for PRANDTL's inspiration in 1904 on how to avoid the difficulties of fully rigorous treatment by introducing the boundary layer concept, the progress in many problems of aerodynamics would have been vastly slower than actually achieved as a result of a constant interplay of experiment and theoretical ideas.

It is also quite likely that a rigorous treatment of turbulent diffusion would be highly complex and in most of the atmospheric pollution applications turbulent diffusion, *per se*, is as we have already seen only a part of the problem.

In certain circumstances a high degree of complexity can be tolerated—the astronomer E. W. BROWN, for example, in compiling tables of the Moon's motion took account of 1500 terms in his final equations. As there is a reasonable assurance that the solar system will long persist in its present form this was not a purely academic feat. But an expression for the diffusion of effluent from a chimney in as many as 15 terms would almost certainly be worthless; it would never be practical to have sufficient quantitative knowledge of many of the factors entering into the problem for the results to be better than those given by much rougher estimation. Such apparently obvious considerations appear sometimes to be overlooked.

It is recorded of R. J. MITCHELL (best remembered as the designer of the Spitfire) that he distrusted complex theory leading to highly involved calculations; they so easily prove misleading. He would say (no doubt with the normal amount of exaggeration for emphasis) that unless an estimation can be done in a few minutes it is not worth doing and that practically any result can be obtained with sufficient accuracy by approximation.

This is not to say that much careful work is not needed to get a physical insight into the general influence of the many factors entering into complex problems. In this way it is possible to achieve a useful appreciation of the important factors and their probable effects on any particular occasion and, equally important, a knowledge of what may safely be neglected.

SOME SEMI-EMPIRICAL METHODS

From what has been recounted above it will be seen that a number of very promising ideas have, as yet, yielded rather small dividends when applied to atmospheric diffusion. But to give a reasonably balanced account it may be as well to mention briefly some of the semi-empirical approaches which have been pressed into service and have, on the whole, performed rather better than might be expected in view of the notorious difficulties associated with turbulent phenomena.

In 1930 SUTTON appreciated that TAYLOR's remarkable theorem (see equation 1)

should be capable of exploitation to give a more logical treatment of atmospheric diffusion than had at that time emerged from analyses in terms of Fickian K values. He was handicapped by a complete lack of observational material on the Lagrangian correlation $R(\xi)$ but, by making physically plausible assumptions and appealing to the vertical profile of wind velocity (the form of which is governed by the downward diffusion of momentum) he was able to fix certain parameters and develop formulae which have proved of considerable value. Sutton effectively assumed a form of the eddy spectrum and the way it should change with stability to harmonize with the accompanying variations in the wind profile and the general level of turbulence.

Most quantitative observational material on atmospheric diffusion is for emissions of suitable gases at ground level with chemical samplers distributed around arcs at various distances downwind of the source. Vertical arrays of samplers on poles were also used less frequently. For near neutral conditions the degree of agreement between SUTTON's formulae and the mean of a large number of trials is indicated below:

	Calculated	*Observed*
Width of cloud at 100m arc	34m	35m
Height „ „ „	10m	10m
Rate of decrease of peak concentration with distance x for a point source	$x^{-1.75}$	$x^{-1.8}$
Rate of decrease of concentration from long cross-wind line source	$x^{-0.87}$	$x^{-0.9}$

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The agreement shown is partly a result of the formulae having been tailored to fit the 100m results, but the agreement between calculated and observed variations with distance is good and SUTTON's treatment has generally been found to serve quite well over a moderate range of the variables. It somewhat underestimates the variation with atmospheric stability.

For the particular case of the vertical diffusion of material from ground sources it was later found that a semi-empirical treatment simpler than SUTTON's could be made solely in terms of the observed variation of wind with height in the lowest few metres above ground. This formulation is free from adjustable constants and gives moderately realistic results in comparison with observation as shown in Fig. 7.* This figure is given not only to show the degree of success which may be obtained with rather crude treatments of essentially complex problems, but to illustrate once more the great influence of stability (i.e. vertical temperature gradient) on diffusion in the lower atmosphere.

These methods which use, to greater or less extent, the variation of wind speed with height to give a measure of the intensity of turbulent exchange, useful though they have been in default of better, suffer from a practical defect in that interpretation of the wind profile is often somewhat ambiguous. This arises from the fact that a large wind shear may arise in two ways—either from a large frictional drag of the wind over the ground (a large surface roughness) or with a quite small surface friction by a markedly stable stratification. The rate of diffusion would, of course, be very much greater in the first case than the second, but uncritical applications of the above treatments would not make the proper distinction.

* It probably has the failing, however, of glossing over the difficulty associated with the diffusivity varying with the scale of the diffusion, and encouraging extension to inappropriate conditions.

It was good to note at the recent Oxford Symposium on Atmospheric Diffusion and Air Pollution that much more attention is now being given to the measurement of intensities of turbulence because the same degree of ambiguity does not exist with these as with the wind profile. A high intensity of turbulence may be either the result of large surface roughness or of large instability (or both), but in either case it will result in a high rate of diffusion as indicated by TAYLOR's expression (see equation

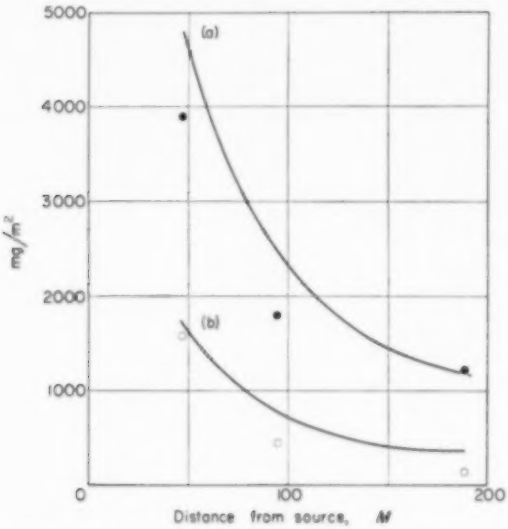

FIG. 7. The concentration at ground level (integrated across the full cloud width) at various downwind distances from a point source of 1 kg/min of gas emitted at the surface. The observation points are shown in relation to theoretical values (full lines). Site: open grassland.
(a) Slightly stable conditions (early evening).
(b) Strongly unstable conditions (summer midday).
Wind speed 3·5 m/sec at 4m height in each case.

1). There will be differences in spectral distribution of the turbulent energy in the two cases, it is true, i.e. different time variations of $R(\xi)$, but we may hope eventually to be able to make allowance for these in terms of a suitable stability parameter.

One of the more valuable results of the extensive studies of wind structure made in the last 20 yr is the better understanding which has been gained as to the mode of operation of the buoyancy forces arising from the vertical temperature gradient in promoting or damping out turbulence. As this is of great significance in air pollution problems, it is considered in some detail in the following section.

THE ROLE OF ATMOSPHERIC STABILITY

To gain some insight into the part played by atmospheric stability it is useful to consider a steady flow in the layer from the ground surface up to some height Z of the order of 50m. It will be supposed that the shearing stress τ and vertical flux of heat H are constant with height in this layer, a reasonably good approximation on most occasions. If U is the mean wind velocity at height Z then the rate of working by the shearing stress is τU, and this is the rate at which energy of the mean flow is

being converted to turbulent kinetic energy in this layer.* The vertical heat flow, H, also produces an input of energy to the turbulence (positive if H is upward, negative if downward); this is because air warmed at the surface becomes lighter and moves upwards through the layer. H units of heat transferred from the surface to mass M of air raises its temperature by an amount ΔT equal to $H/(MC_p)$ where C_p is the specific heat of air at constant pressure. The density of this mass of air is changed by the fraction $\Delta T/T$ where T is the average absolute temperature of the air, and this change of density with respect to its environment evokes a buoyancy force of $(Mg\Delta T)/T$ (where g is gravitational acceleration), which therefore equals $Hg/(C_pT)$. If we suppose all the added heat to pass upwards through the layer, as will very nearly be true for fairly steady conditions and not too deep a layer, then H units of heat per unit area traversing the layer each second will result in work being done at the rate $(HgZ)/(C_pT)$. There are therefore two rates at which energy is being supplied to the turbulence in the layer 0 to Z, viz.:

by shearing stress	τU,
by buoyancy	$(HgZ)/(C_pT)$.

When H is small the turbulence in the air is preponderantly of dynamical origin (i.e. produced by the shear) and the heat transfer will be by the process known as forced convection. On the other hand if τU is nearly zero then the transfer of heat is solely effected by motions arising from buoyancy—a state called free convection. The pattern of the turbulence in the two cases is very different. In the intermediate states a governing parameter for the flow pattern should therefore be the ratio (Rf) of these rates of working, i.e.

$$Rf = \frac{gHZ}{C_pT\tau U}$$

This dimensionless number is therefore expected to play a part rather similar to that of the Reynolds number in non-stratified flow.

RICHARDSON in 1920 introduced a parameter essentially similar to Rf but, as it was not then possible to measure H and τ in the atmosphere, he used instead the related values of the vertical gradients of wind velocity and temperature. Richardson's number is therefore

$$Ri = \frac{g\,\partial T/\partial z}{T(\partial u/\partial z)^2}.$$

It is customary now to call Rf (or variants of it) the flux Richardson number and to insert in its definition a minus sign to make both Rf and Ri positive for stable conditions, negative for unstable.

To demonstrate the value of Rf in co-ordinating observations under various conditions, Fig. 8 has been prepared using the excellent wind structure data obtained at the Brookhaven National Laboratory, Long Island, U.S.A.† (PANOFSKY, 1953; PANOF-

* Provided the shear stress is directly opposed to the mean wind as is approximately the case with the observations dealt with later.

† For flow in the lowest few metres the utility of Richardson numbers is quite well established, but in studies at rather greater heights (diffusion of effluents from high stacks, etc.) their relevance is as yet less appreciated. This is perhaps because $\partial T/\partial z$ and $\partial u/\partial z$ both become too small for accurate measurement at such heights. But if H/τ is really the important consideration, then the ratio $\partial T/\partial z : \partial u/\partial z$ (or the ratio of differences $\Delta T/\Delta u$ over a height interval) *near the ground* should be a good and fairly easily measured substitute except in built-up areas.

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SKY and MCCORMICK, 1954). Values of $\bar{w}/U$ from the 91m level observations are plotted against Rf, $\bar{w}$ being the r.m.s. value of vertical eddy velocity and U the mean wind speed at the same height. On ten occasions values of H and τ were measured so Rf could be evaluated. For another ten periods during which H was not observed the ratio H/τ was taken to be given by $\Delta T/\Delta u$ where

ΔT = potential temperature difference between heights of 11m and 125m.
Δu = corresponding wind speed difference.

Fig. 8 shows there to be an approximately linear variation of $\bar{w}/U$ with $\sqrt{(Rf)}$ and the high correlation coefficient of $-0{\cdot}96$ is very good evidence that one feature at least of the pattern of turbulence is indeed governed by shear and heat flux in the manner discussed above and that the consideration of stability effects in terms only of the vertical temperature gradient (a frequent practice) is defective.

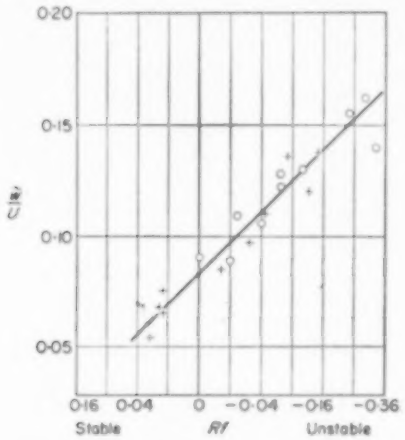

FIG. 8. The relative intensity of the vertical turbulence ($\bar{w}/U$) at a height of 91m related to the flux Richardson number as a measure of stability. Circled points are for Rf calculated using measured values of heat flux and shearing stress; crosses for the other runs for which only wind and temperature profile data are available. Range of wind speed 3·5 to 15 m/sec.

The decrease in the level of turbulence in stable conditions is a result of work done by the turbulence in pumping heat downwards in opposition to the buoyancy forces. Fig. 8 suggests that with increasing stability a stage might be reached when $\bar{w}/U$ would become zero corresponding to streamline flow. RICHARDSON in his classical work on this subject deduced that the change from streamline to turbulent flow should occur at a critical Ri of unity. Both theory and observation have subsequently tended to show that turbulence in a boundary layer dies out at some rather lower critical Richardson number than unity, but no definite criterion has so far been established. Here again a consideration of the flux Richardson number makes it clearer what the difficulties are. Rf varies with the depth of layer considered: for a shallow layer of air adjacent to the ground Rf is small, showing that the effect of the heat flux through this layer on the flow in it is slight (a fact verified by observation), and it follows that turbulence there will be less easily suppressed than at greater

heights. Furthermore as long as turbulence does persist near the surface some turbulent energy is likely to be transferred upwards, to hamper the establishment of truly non-turbulent flow at the higher levels.

An observational difficulty in studying the more strongly stable conditions is the increasing emphasis which is placed on the high frequency end of the eddy spectrum. It was instrumental response limitations which prevented the Brookhaven work being extended to greater stabilities than shown in Fig. 8, and elsewhere experience has been similar; equipment designed in the first place to be suitable for daytime studies is not responsive enough at night. From the atmospheric pollution viewpoint the study of the structure of turbulence needs to be extended to highly stable conditions for obvious reasons. It is to be hoped that more effort may be channelled in this direction now that unstable conditions have been, if not well explored, at least successfully reconnoitred.

Buoyancy has a further action whenever the emission of diffusing material is accompanied by a marked release of heat. With factory chimneys this has the beneficial effect of increasing the effective height, a matter of considerable importance to nuclear energy power stations in particular.

The behaviour of buoyant plumes in the atmosphere and other more general aspects of buoyant motion in the atmosphere have been given considerable attention in the last few years and some useful foundations laid. On the basis of this work, which it is beyond the scope of this article to do more than mention, semi-empirical formulae describing the behaviour of hot chimney plumes have been derived. One or two of the latest of these appear to take account of the more important effects in a physically reasonable manner, but at present the range of published observational data is rather too small to give much indication of the relative merits of the various treatments or to give the mathematical physicist enough pabulum to be very stimulating.

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The importance of securing enough observational material can hardly be overstressed. The nature of problems involving atmospheric turbulence is such that, to use the communications engineer's term, the signal to noise ratio is usually rather low. To disentangle useful signals many data are needed, and furthermore a large range of the variables under investigation must be covered.

It may be worth underlining this last point by recalling a striking example of its being neglected. The author was astonished on one occasion in the war years when he saw that a statistical examination of a mass of data on the night-time variation of wind speed with height in the lowest 100 ft in London parks produced the remarkable result that no significant effect of the vertical temperature gradient could be demonstrated! Further research into the report threw a ray of light on this apparently rather suspicious behaviour of the atmosphere in London parks. The data had been gathered, almost *in toto*, on windy overcast (and therefore air-raid free) winter nights! Similar, if less extreme, (but less excusable) examples of inadequate exploration of the reasonably accessible range of variables have been noticed on more than one subsequent occasion.

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Letters to the Editors

Computation of pollution from several sources

THE study by D. H. LUCAS (1958) of " The atmospheric pollution of cities " is both interesting and timely. Applications to an entire city of the quantitative methods of dispersion analysis that have proved so effective in connection with isolated pollution sources have been surprisingly few. Doubtless, the reason lies, to a considerable extent, in the awkwardness of the area source dispersion formulae that arise, and the labor of the numerical computations involved. Mr. LUCAS suggested a simplified formula to describe urban pollution that seems to work very well. The purpose of this letter is to suggest an alternative computational approach that may have some advantages.

The area source dispersion formula is obtained by summing the point source formula over all sources (chimneys). In practice, Mr. LUCAS has instead distributed the total estimated SO_2 emission uniformly over a hypothetical city and integrated the point source dispersion formulae with respect to x and y, which is equivalent. In either event, one arrives at a formula for the concentration at a point (x, y) due to the urban area pollution source. What I would like to point out is the possible computational advantage to be gained by regarding the problem just *backwards*.

Numerically, it comes to exactly the same thing if one calculates the concentration at a point (x, y) from a number of arbitrarily distributed sources of equal strength, at equal elevation h; or if one calculates (after reversing the mean wind direction), for a single source located at point $(x, y; h)$ and of strength equal to the *combined* strength of the actual sources, the *summation* of concentrations that would result at the various actual source locations. A convenient way to do the actual computa-

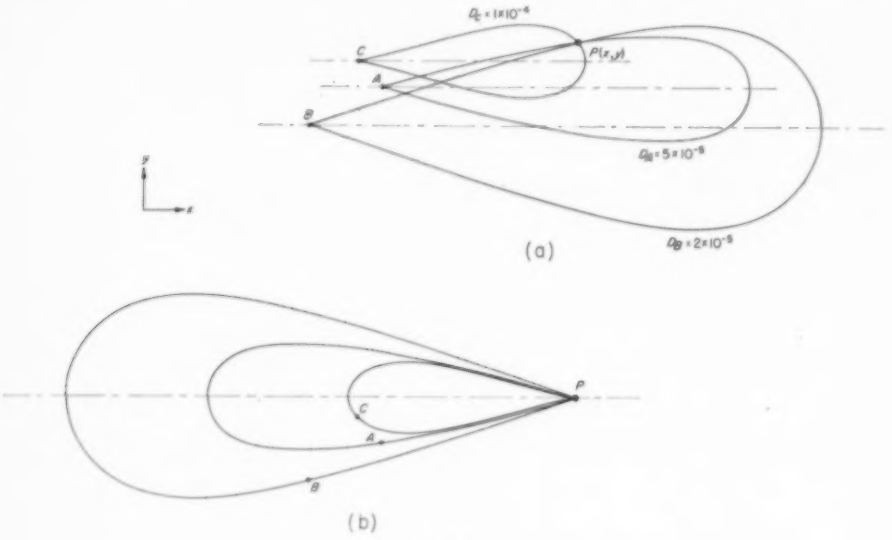

FIG. 1

tions would be, first, to prepare a map of the city with source strengths indicated, either as actual point sources, or as weighted averages over convenient small areas. Then, transparent plastic overlays of the ground level, point source concentration distributions for various meteorological situations (and, if necessary, various source heights) and unit source strengths could be prepared. [Numerical evaluation of point source dispersion formulae is facilitated by use of various nomograms; cf GIFFORD (1953), (1956), and U. S. WEATHER BUREAU (1955)]. The concentration at point (x, y) due to the urban (area) source is then found by selecting the appropriate point source overlay, orienting it over the city map with its *origin* at the receptor point (x, y), and extending *upwind*, and adding up all the

pseudo-point source concentration values at the actual point or small area source locations, weighting (multiplying) each by its individual strength. Actually, this procedure will go a step farther than that carried out by LUCAS, in that allowance for a non-uniform area distribution of source strengths has been made.

As an illustrative example, consider the ground-level concentration at a point $P(x, y)$ due to three continuously emitting sources of pollution located (as in Fig. 1) at points A, B and C, having strengths Q_A, Q_B and Q_C, at height h. The computation of the dosages at P, due to all three of these sources, ordinarily proceeds (in effect) by determining the value of the relative concentration isopleth D passing through each point, multiplying each by the corresponding source strength, and summing; i.e.

$$\text{Dosage at } P = D_A \cdot Q_A + D_B \cdot Q_B + D_C \cdot Q_C$$

If the sources at A, B and C have strengths of, say, 1, 2, and 3 g/sec, then (for the relative concentrations indicated in Fig. 1(a)),

$$\text{Dosage at } P = 1 \times 5 \times 10^{-5} + 2 \times 2 \times 10^{-5} + 3 \times 10^{-4} = 3{\cdot}9 \times 10^{-4} \text{g}^{-3}$$

In Fig. 1(b), exactly the same three relative concentration isopleths appear; but each now originates at point P, and is directed *upwind*. The skeptical reader can convince himself, by a moment's work with a scrap of tracing paper, that in fact exactly the same isopleths do pass through points A, B and C (and consequently that the total dosage is the same). Since these source points have been located arbitrarily and asymmetrically, relative to the receptor point P, the process will work for any number of sources of arbitrary strength, arbitrarily located. A uniform source height was assumed; practically it might be convenient to group a large number of sources according to height categories. Also it might be convenient to group sources into limited areas, and assign their combined strength to some representative point in the area. It seems that the problem of area source pollution computations could be considerably simplified by such short-cuts.

The writer has to admit that he has not yet had occasion to test this method, but offers it as a suggestion that seems promising, particularly for hand computations. Regardless of computational method, there can be no doubt of the importance of more quantitative urban pollution studies, such as that by D. H. LUCAS.

FRANK GIFFORD

Meteorologist in Charge
Weather Bureau Office
Oak Ridge, Tennessee
U.S.A.

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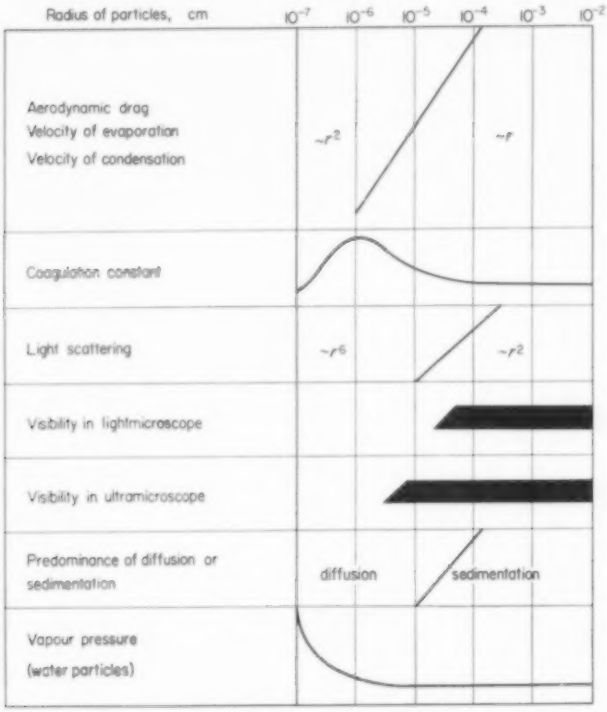
Book Reviews

N. A. FUCHS: **Mekhanika aèrozolei (The Mechanics of Aerosols)**. Publishing Office of Akademia Nauk, Moscow, 1955. 351 pp. (In Russian.)

THE book by FUCHS may be considered the first theoretical monograph on the physics of aerosols in general. The term " mechanics of aerosols " itself appears in the literature for the first time, and I think, justly. By the phrase aerosol mechanics FUCHS means the study of laws of motion of aerosol particles, their sedimentation and coagulation, as well as their motion in various force fields. The forces acting on the aerodispersion system he divides into three categories: exterior forces (the action of force fields), the resistance of a medium, and the forces of mutual action among the particles.

The author divides the subject matter of his book into eight chapters. The first one he devotes to the classification of aerosols and to the dimensions and forms of aerosol particles. A division

TABLE 1



according to the occurrence, into fog, fume, dust, smoke, etc., is just as inappropriate as are all divisions in other monographs on aerosols. The classification according to the physical and physical–chemical characteristics is to a certain extent new, and has many advantages because various categories of classification very often have different physical–chemical characteristics.

Among aerosols, i.e. among aerodispersing systems of solid and liquid particles in a gas medium he places systems with particle size of the order 10^{-7} to 10^{-1} cm. Thus, contrary to all other authors, he shifts the upper limit higher by two orders. According to the sizes he divides aerosols into fine-dispersing, middle-dispersing and coarsely-dispersing. The fine-dispersing aerosols or highly dispersing aerosols behave like a sphere of particle-dimensions smaller than 0,5–1,10^{-6} cm. The middle-

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dispersing aerosols with transient characteristics are like spheres of particle-dimensions of the order 10^{-5}–10^{-6} cm. Aerosols with particles larger than 10^{-4} are coarsely dispersing aerosols. The characteristics of the various categories are easily seen from Table 1. Equations of all kinds of dispersing curves and laws of dispersion are derived in detail.

In the second chapter the author treats the equal straight-line motion of aerosol particles, i.e. the influence of the resistance of the medium to particles of various sizes (the Stokes, Cunningham, Osseen and Goldstein laws). He analyses the motion of non-spherical particles, the motion and the resistance of a medium to liquid aerosols and the falling out of the small drops from clouds. Further on he discusses motion of aerosol particles in confined spaces, motion in vertical as well as in horizontal electric fields, and finally he describes and analyses thermophoresis.

In the third chapter, he describes rectilinear motion of unequal aerosol particles. He occupies himself with straight-line motion with different values of *Re*, with the oscillation of particles in an acoustical field, and with the dispersion and absorption of sound waves by an aerosol cloud. Further on he describes the action of hydrodynamic forces upon particles and the electrostatic dissipation of particles in an aerosol cloud.

The fourth chapter is dedicated to the curved motion of aerosol particles. Here the author investigates the curved motion of particles in a horizontal alternating electric field, sedimentation of aerosols from laminar flow by gravitation, sedimentation in an electric field, accelerated sedimentation in centrifugal fields (aerosol centrifuge, cyclones, etc.). He also analyses theoretically different modes of taking aerosol samples.

Brownian motion and the diffusion of aerosols are described in the fifth chapter. Diffusion is also treated in different aerodynamic conditions and at large *Re*, together with the theory of diffusion in textile and fibre filters. Not even the retention of aerosol particles in respiratory sysems has been omitted.

The whole of Chapter VI is devoted to convection and turbulence in an aerosol cloud. The author treats the motion and sedimentation of particles in the turbulent flow, and diffusion and sedimentation in the atmosphere.

The whole of Chapter VII is devoted to coagulation of aerosols. He discusses the technique of coagulation of spherical and non-spherical particles, electrically charged as well as uncharged, coagulation in an electric field, coagulation in an ultrasonic field, and finally the coagulation during sedimentation and in turbulent flow.

In the eighth and last chapter, the author gives information about his theory of preparation of solid aerosols from powder materials.

The book is not only a good lecture-book of mechanics of aerosols but also an indispensable hand-book for all who occupy themselves with basic and applied research of aerosols, air pollution, industrial dust, microphysics of clouds, etc. It is only a cause of regret that a book of such world-wide importance has been published only in the Russian language and is therefore accessible only to a limited number of specialists.

K. SPURNÝ

N. A. FUCHS: **Isparenie i rost kapel' v gazobraznoi srede (The Evaporation and Growth of Drops in the Gas Medium)**. Itogi nauki Akademia Nauk, Moscow, 1958. 90 pp. (In Russian.)

THE whole monograph critically analyses the results of theoretical and experimental work, old and new, which deals with coagulation and growth of aerosol drops in a gas medium. The author especially and generally compares the results of theory and experiment. The matter of the book is divided into three chapters. The first one, which comprises more than half of the book, describes the quasistationary evaporation and the growth of drops which are at rest relative to the medium. He derives the Maxwell relation (1877) for evaporation of spherical droplets and similar theories by Sreznevsky (1882) and Nestle (1932).

He also analyses the influence of the hydrodynamic flow upon the evaporation rate and derives the evaporation rates (Stefan, 1881) for spherical as well as for non-spherical drops.

He analyses in detail Langmuir's theory (1915) concerning the influence of concentration gradients at the surface of a drop upon the evaporation rate, and also analyses the thermodynamics of evaporation, i.e. the reduction of temperature of still and moving drops. He studies the evaporation rate of

drops larger than the mean free path of molecules ($r \gg l$) and of drops approaching the size of the mean free path.

He summarizes the results of much experimental work and compares them with theoretical values.

The second chapter he devotes to the quasistationary evaporation and growth of drops moving through a gas medium. He again compares the results of theory (his own and those of other authors) with experimental results.

The third chapter deals with non-stationary evaporation and the growth of drops, both undisturbed and moving.

Several special recent works on the kinetics of evaporation (1950–54) are discussed.

The monograph is a valuable hand-book for all experts in the field of liquid aerosols and it is especially valuable for the correlation of various theoretical and experimental results.

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PAPERS ACCEPTED FOR PUBLICATION

A. J. HAAGEN-SMIT, VINCENT D. TAYLOR and MARGARET F. BRUNELLE: Spectroscopic analysis of industrial emissions for nitric oxide, nitrogen dioxide and sulfur dioxide.

BERT BOLIN: Note on the exchange of iodine between the atmosphere, land and sea.

ROBERT A. BAKER and ROBERT C. DOERR: Methods of sampling and storage of air containing vapors and gases.

WILLIAM P. ELLIOTT: The areas within concentration isopleths downwind of continuous point source.

WILFRED NIELS ARNOLD: The longevity of the phytotoxicant produced from gaseous ozone–olefin reactions.

J. PEMBERTON, MARJORIE CLIFTON, J. K. DONOGHUE, D. KERRIDGE and WINIFRED MOULDS: The spatial distribution of air pollution in Sheffield, 1957–1959.

MARJORIE CLIFTON, J. K. DONOGHUE, D. KERRIDGE, WINIFRED MOULDS and J. PEMBERTON: The reliability of air pollution measurements in relation to the siting of instruments.

GEORG HUGO NEUMANN, STIG FONSELIUS and LARS WAHLMAN: Measurements on the content of non-volatile organic material in atmospheric precipitation.

GEORGE EVAN MOORE and MORRIS KATZ: Polynuclear aromatic hydrocarbons in the particulates of diesel exhausts in railway tunnels and in the particulates of an urban atmosphere.

E. SAWICKI, W. ELBERT, T. W. STANLEY, T. R. HAUSER and F. T. FOX: The detection and determination of polynuclear hydrocarbons in urban airborne particulates—I. The benzopyrene fraction.

E. SAWICKI, T. R. HAUSER and T. W. STANLEY: Ultraviolet, visible and fluorescence spectral analysis of polynuclear hydrocarbons.

JEROME F. THOMAS, BERNARD D. TEBBENS, ELDON N. SANBORN and JAMES M. CRIPPS: Fluorescent spectra of aromatic hydrocarbons found in polluted atmospheres.

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Int. J. Air Poll. Pergamon Press 1959. Vol. 2, pp. 115–126. Printed in Great Britain.

THE AREAS WITHIN CONCENTRATION ISOPLETHS DOWNWIND OF CONTINUOUS POINT SOURCE

WILLIAM P. ELLIOTT
Geophysics Research Directorate,
Air Force Cambridge Research Center
(*Received* 6 *March* 1959)

Abstract—Empirical formulae for estimating the area covered by concentrations of gas equal to or exceeding a given value are presented. These formulae are derived from regression lines of the value of the logarithm of the area against the logarithm of the critical concentration divided by the source strength and the logarithm of the concentration divided by the source strength and multiplied by the wind speed at 2 m. The scatter about the regression lines is reduced if one stratifies the entire sample by means of certain parameters. These parameters are: stability ratio, a measure of the atmospheric thermal stability which is the difference of the temperatures at 4 m and $\frac{1}{4}$ m divided by the square of the wind at 2 m; the temperature difference alone; and the standard deviation of the horizontal wind direction. The first parameter was found to reduce the scatter the most and the last parameter reduced the scatter the least. The results are presented in the form of tables of the regression coefficients and illustrated in a graph (Fig. 3). Generally speaking it is found that the logarithm of the area, A, was linearly related to the logarithm of the concentration, χ, divided by the source strength, Q, and multiplied by the wind speed, u, in the form $\log A = a \log (\chi u/Q) + b$. When the variables are expressed in c.g.s. units a varies from about $-0{\cdot}6$ to $-1{\cdot}2$ and b varies from about 2 to 7 as the atmosphere passes from unstable to stable.

The data used to arrive at these results were taken over level prairie land with short grass. The tracer was sulfur dioxide emitted continuously from a point source about $\frac{1}{4}$ m from the surface. Measurements were out to a distance of about 800 m from the source.

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1. INTRODUCTION

DURING the summer of 1956 the Geophysics Research Directorate of the Air Force Cambridge Research Center sponsored and directed Project Prairie Grass, a field study of the diffusive power of the atmosphere. The data taken during Project Prairie Grass can be analyzed from a number of viewpoints. The data have been used to evaluate SUTTON's diffusion equations (BARAD and HAUGEN, 1959) and a forthcoming paper will discuss the Calder–Deacon formulation in light of these data. However, one is frequently concerned with the problem of estimating how large an area will be affected by dosages of a given critical value. It may be of greater interest, say, to a farmer to know directly how much of his crops may be subjected to a toxic dose of some contaminant than to be able to specify the peak concentration and point values of concentration over his fields. It is to this problem that this paper is directed, i.e. to determine the area which will be subjected to concentrations equal to or greater than a specified value, and, perchance, to discover some of the meteorological factors influencing this area.

The participants in Project Prairie Grass were a group from the Massachusetts Institute of Technology who made the diffusion measurements and some meteorological measurements, and groups from the Texas A & M Research Foundation, the University of Wisconsin, the Air Weather Service and the Air Force Cambridge Research Center. The data used in this study were taken mainly from the work of the first two groups.

For the purpose of a brief subject orientation a short description of the observational site and procedures will be given. Further details can be found in BARAD and HAUGEN (1959) and a complete description in BARAD (1958).

2. FIELD SITE AND OBSERVATIONAL PROCEDURES

The field work was conducted over a flat prairie in north central Nebraska near the town of O'Neill. At the beginning of the program the uniform grass ground cover was mowed to a height of about 5 cm and during this test period little growth change occurred.

Sulfur dioxide was used as the tracer element. It was emitted for 10 min at a height of 46 cm during sixty-four gas releases and 150 cm during six releases. The source was located at the center of five concentric circles with samplers placed only on the northern semi-circles. The five circles had radii of 50, 100, 200, 400 and 800 m. The samplers were exposed every 2° of arc on the four inner arcs and every 1° on the outer arc. All samplers were 1·5 m above the ground. Most of the meteorological measurements were made a short distance beyond the 800 m arc. Thirty-four of the seventy gas releases emitted during July and August were made during lapse conditions and thirty-six during inversions.

The samplers were midget impingers aspirated by means of electrically operated vacuum units. During the experiments air was drawn into the impingers and bubbled through a dilute hydrogen peroxide solution. The sulfur dioxide in the sample combined with the hydrogen peroxide to form sulfuric acid. The average gas concentration was then determined from measurements of the electrical conductivity of the final solution.

3. COMPUTATION OF AREAS

The first method used to obtain areas was based upon fitting a Gaussian curve to the concentrations observed along each arc. Only those gas releases, whose arcwise distribution of gas concentration was approximately normal, were used. In effect, this means that the skewness did not exceed 0·37 and the kurtosis was between 2·4 and 3·6 for each arcwise distribution of concentration. By and large the most nearly normal runs were found at night. A Gaussian curve was fitted to each arc of the chosen runs. The peak values of concentration along the fitted curves for the 800, 400 and 200 m arcs were selected as the values of the isopleths whose enclosed areas were to be found. At each arc the distance of the particular isopleth from the axis of peak concentration was found by using the fitted normal curve. These ordinates were plotted and a closed curve drawn through the points. The enclosed area was then obtained by using a planimeter.

In all, twenty-eight runs, or 40 per cent of the total, satisfied the normality criteria. Of these, ten were daytime runs and eighteen were nighttime. About one-third of the day runs and one-half the night runs were " normal ".

A second and more direct method of computing the areas was also used. The observed concentrations were plotted on a grid and the isopleths of the observed peak concentration along the 800, 400 and 200 m arcs were drawn and the enclosed area measured with a planimeter. No restrictions were placed on the degree of normality exhibited by the concentration data. Of the seventy runs made, sixteen were not used for the following reasons:

seven because of various equipment malfunctions;
six because of extremely light and variable winds or mean wind direction shifting during release;
two because there were no concurrent meteorological data;
one because of extreme stratification of cloud where the cloud remained below the samplers for part of the distance.

Therefore, in all, fifty-four gas releases were utilized, or about twice the number of " normal " runs.

A certain amount of subjectivity obviously enters into the drawing of the isopleths, particularly for the non-normal runs. Examples of observed patterns are shown in Figs. 1(a) and 1(b). Fig. 1(a) shows the patterns obtained from run 17. This run was made about 2000 CST and it is one of the runs whose distributions were nearly normal. The patterns are quite typical of these " normal " runs showing an elongated cigar shape with the maximum width occurring about halfway between the end points. The data points are shown as dots in the drawing. Fig. 1(b) shows the patterns obtained from run 25. This run was made about 1300 CST and it is one of the least normal. It illustrates the difficulties in precisely defining the shape of the isopleth. Close examination of the actual data reveals that the small wiggles in the line are probably real, since they can be found in data from several arcs. It appears that these patterns are made up of a number of the cigar-shaped areas (as shown in Fig. 1(a)) at various angles to each other. Youthful enthusiasm and a certain amount of brashness were a great help in drawing the patterns illustrated in Fig. 1(b). Nevertheless, subsequent results indicated that a fair degree of reliance could be placed in those areas in spite of the uncertainties inherent in their determination.

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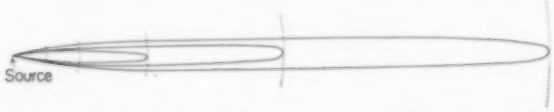

FIG. 1(a). Isopleths for peak concentrations at 800, 400 and 200 m, 23 July 1956, 2000 CST.

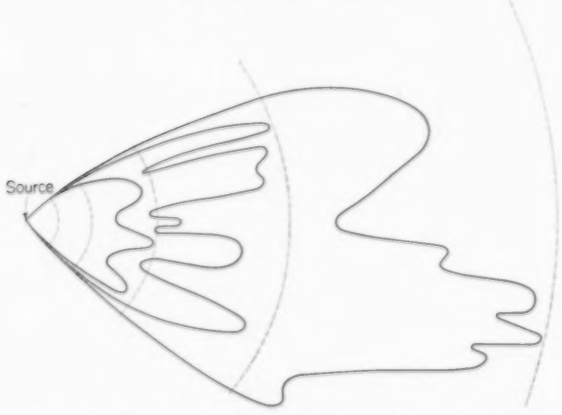

FIG. 1(a). Isopleths for peak concentrations at 800, 400 and 200 m, 1 August 1956, 1300 CST.

In the following evaluations, the areas found by this more direct method will be

used in preference to those determined from the fitted normal curves. Since the assumption of normal distributions of concentration along the arcs forms the basis for a number of theoretical diffusion studies the first attempts at estimating the areas were confined to the near normal cases. However, normality did not appear to be a crucial assumption for this particular study. Twice as many runs could be incorporated into the study if the normality restrictions were dropped and it did not appear that any bias was introduced by incorporating the non-normal runs into the prediction schemes which will be described later. When all the runs were used, no significant differences between the two sets of results could be found except in so far as "normality" appeared more common at night.

4. ESTIMATION OF AREAS

This section will compare various methods of estimating the areas within isopleths of concentrations. The results will all be empirical formulae derived from the observations. No other data will be employed to test the results; therefore the formulae must be considered tentative until similar independent observations can be made. The method will be to obtain linear regression lines of the common logarithm of the area versus the common logarithms of two parameters with the data stratified in several different fashions. The standard errors of estimate of the several regression lines will be compared and these comparisons will form the basis for conclusions regarding the applicability of the parameters used. Where the data have been divided into class intervals the standard error of the overall grouping has been determined by combining the standard errors (adjusted for differences in sample size) of the respective classes.

The area within an isopleth of concentration should be related to the value of the isopleth itself. Thus, the first step was to plot the logarithm of the area enclosed by an isopleth whose value was the peak concentration along a particular arc against the logarithm of the value of that isopleth divided by the source strength (since different source strengths were used for different runs). The symbol A will be used to designate the area; χ to designate the concentration and Q to designate the source strength. The units of A are square meters, χ is in units of milligrams per cubic meter and Q in milligrams per second. Thus χ/Q has the units seconds per cubic meter.

The correlation coefficient between log A and log χ/Q was $-0{\cdot}88$ and the resulting linear regression line showed a standard error of estimate of 0·25. Since the standard errors (hereafter abbreviated SE) express the deviation of log A from their predicted value, we still need some expression of the deviations of the areas from their predicted value. If the errors are normally distributed about the regression line we can say that

$$10^{-SE} \leqslant A_p/A_o \leqslant 10^{SE} \tag{1}$$

about 68 per cent of the time. A_p is the area predicted by the regression line and A_0 the observed area. The interval defined by equation 1 will be designated by the symbol I. When SE = 0·25, I is 0·58–1·78. We should be able to improve this by introducing some meteorological parameters.

The first meteorological parameter introduced was the mean wind speed u. Fig. 2 shows log A plotted against log $\chi u/Q$, u being taken as the 2 m wind speed. The distances from the source at which the particular values of $\chi u/Q$ were found are indicated in the graph. The underlined points are the observations from those runs

which were approximately normal according to the criteria first given. The linear correlation coefficient between the two variables is −0·92. A linear regression line was fitted to the data and SE for this line was found to be 0·21 which corresponds to an I of 0·61–1·63. The introduction of the wind speed has evidently reduced SE somewhat but greater improvement can be hoped for by the introduction of further parameters.

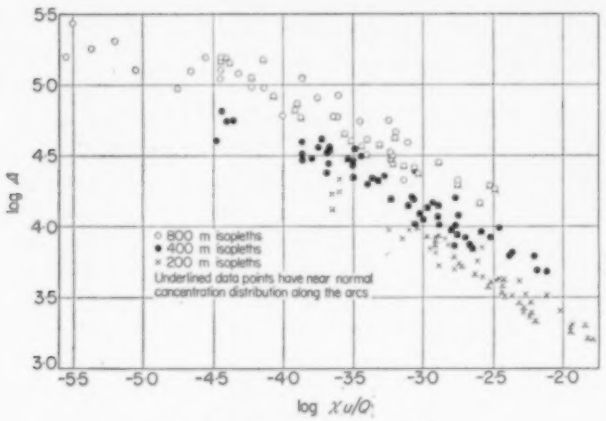

FIG. 2. Log A versus log $\chi u/Q$.

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In most studies of atmospheric diffusion it is found that atmospheric thermal stability plays an important role in the diffusion processes (for example, see SUTTON (1951)). It is logical to expect stability to be an important factor in the determination of the area. The choice of a suitable stability parameter is not quite so simple. The simplest measure of stability is the lapse rate; therefore the first stability parameter tried was the temperature difference between 4 m and 0·5 m.

The data were first split into two groups depending on whether the temperature difference was negative (lapse condition) or positive (inversion condition). SE for this scheme is 0·18 and I is 0·66–1·51. This further reduction was encouraging and the data were further subdivided into three and into six stability classes. For the data split into three classes SE was 0·17 and for six classes SE = 0·13. The three classes seem little better than two but the six class division shows an obvious improvement.

Another stability parameter which has found favor with some workers is the so-called stability ratio. This parameter is defined as

$$\mathrm{SR} = \frac{T_{4\cdot0} - T_{0\cdot5}}{U_2^2} \times 10^5 \ ^\circ\mathrm{C}/(\mathrm{cm/sec})^2 \tag{2}$$

where $T_{4\cdot0} - T_{0\cdot5}$ is the temperature difference between 4·0 m and 0·5 m and U_2 is the wind speed at 2 m. SR is obviously related in form to the Richardson number.

The log A– log $\chi u/Q$ data were split into three and into six classes with SR as the stratifying parameter. SE = 0·16 for the three class division and 0·10 for the six class division. These give I as 0·69–1·45 and 0·79–1·26 respectively. This latter value represents an appreciable decrease in I over the simple lapse rate case.

In the last schemes the value of the wind speed appears in two places, in the term $\chi u/Q$ and in SR. It is pertinent to inquire whether χ/Q would have done just as well if SR was used as the stability parameter. When the log A versus log χ/Q data were stratified by SR into three and six classes the resulting SEs were 0·18 and 0·12 respectively. Evidently the introduction of wind speed in both places produces a better estimate of the area in either case than if it were left out.

Another parameter which was been introduced into the study of diffusion is the standard deviation of the azimuth angle of the horizontal wind component (CRAMER *et al.*, 1958). This parameter was computed from observations made by them at the Prairie Grass site. If the log A vs. log χ/Q relationships are computed using this parameter (denoted by σ_a) the results are as follows: data divided into two classes, SE = 0·23; into three classes SE = 0·22; into six classes SE = 0·20. SEs are larger for this parameter than for the corresponding ones computed with either lapse rate or stability ratio. If the log A versus log $\chi u/Q$ data are grouped by σ_a some improvement is seen. SE = 0·18 for the data split into two classes, 0·17 for three classes, and 0·15 when split into six classes. It would appear from this analysis that σ_a is not so good a parameter as the stability parameters mentioned above for estimating the area.

By this time the reader has probably experienced difficulties in keeping the numbers in mind. Table 1 summarizes the limits of each of the various classes and gives the number of independent observations in each class. Table 2 presents a summary of the results so far. Column I lists the parameter used to stratify the data, column II gives the number of classes into which the data were stratified, column III assigns an index number to the class. The most unstable class is listed first and the most stable last in the case of the stability parameters, while the σ_a classes are listed in the order of decreasing values of σ_a. Column IV gives the results for log A versus log χ/Q with IVa the correlation coefficient, r, IVb lists SE and IVc lists I. Column V gives the same information as IV for the log A versus log $\chi u/Q$ lines. r, SE and I are listed for each of the regression lines and SE and I were also computed for the total prediction schemes based upon the various divisions. These are found in the appropriate rows labeled Total.

TABLE 1

Class number	Lapse rate range	No. of observations	SR range	No. of observations	σ_a Range	No. of observations
1	⩽ −2·20	8	⩽ −0·70	8	>12·0	9
2	−1·72→−2·19	9	−0·69→−0·35	9	12·0→10·0	8
3	−1·71→0·0	9	−0·34→0·0	9	10·0→ 7·3	9
4	0→0·45	9	0·0→0·20	9	7·3→6·0	9
5	0·45→0·80	10	0·21→0·85	10	6·0→5·1	9
6	>0·81	9	>0·86	9	<5·1	9
1	< −1·71	17	< −0·35	9	>10·0	17
2	−1·71→0·45	19	−0·34→0·25	19	10·0→6·0	18
3	>0·45	18	>0·25	18	<6·0	18
1	<0	26	<0	26	>7·2	26
2	>0	28	>0	28	<7·2	27

TABLE 2

I Stratification parameter	II No. of classes	III Class number	IV a	IV b	IV c	V a	V b	V c
			r	SE	*I*	*r*	SE	*I*
Unstratified	1	1	−0·88	0·25	0·56–1·78	−0·92	0·21	0·62–1·62
Lapse rate	6	1	−0·95	0·15	0·71–1·41	−0·91	0·20	0·63–1·59
		2	−0·98	0·10	0·74–1·26	−0·98	0·10	0·79–1·26
		3	−0·97	0·12	0·76–1·32	−0·94	0·17	0·68–1·48
		4	−0·96	0·13	0·74–1·35	−0·99	0·06	0·87–1·15
		5	−0·90	0·19	0·65–1·55	−0·97	0·10	0·79–1·26
		6	−0·93	0·18	0·66–1·51	−0·97	0·13	0·74–1·35
		Total		0·15	0·71–1·41		0·13	0·74–1·35
	3	1	−0·95	0·14	0·72–1·38	−0·94	0·17	0·67–1·48
		2	−0·94	0·16	0·69–1·44	−0·94	0·17	0·67–1·48
		3	−0·85	0·25	0·56–1·78	−0·94	0·16	0·69–1·44
		Total		0·18	0·66–1·51		0·17	0·67–1·48
	2	1	−0·96	0·14	0·72–1·38	−0·93	0·19	0·65–1·55
		2	−0·82	0·27	0·51–1·86	−0·93	0·17	0·67–1·48
		Total		0·22	0·60–1·66		0·18	0·66–1·51
SR	6	1	−0·97	0·12	0·76–1·32	−0·96	0·13	0·74–1·35
		2	−0·98	0·08	0·83–1·20	−0·98	0·10	0·79–1·26
		3	−0·98	0·12	0·76–1·32	−0·98	0·09	0·81–1·33
		4	−0·98	0·09	0·81–1·23	−0·99	0·06	0·87–1·15
		5	−0·96	0·13	0·74–1·35	−0·99	0·07	0·85–1·18
		6	−0·95	0·14	0·72–1·38	−0·97	0·12	0·76–1·32
		Total		0·12	0·76–1·32		0·10	0·79–1·26
	3	1	−0·96	0·13	0·74–1·35	−0·93	0·19	0·65–1·55
		2	−0·94	0·16	0·69–1·44	−0·97	0·11	0·76–1·29
		3	−0·85	0·24	0·57–1·74	−0·94	0·16	0·69–1·44
		Total		0·18	0·66–1·51		0·16	0·69–1·44
	2	1	−0·96	0·14	0·72–1·38	−0·93	0·18	0·66–1·51
		2	−0·82	0·27	0·54–1·86	−0·93	0·17	0·67–1·48
		Total		0·22	0·60–1·66		0·18	0·66–1·51
σ_a	6	1	−0·96	0·13	0·74–1·35	−0·94	0·16	0·69–1·44
		2	−0·98	0·10	0·79–1·26	−0·96	0·14	0·72–1·38
		3	−0·88	0·20	0·63–1·59	−0·95	0·13	0·74–1·35
		4	−0·85	0·23	0·59–1·70	−0·95	0·14	0·72–1·38
		5	−0·83	0·23	0·59–1·70	−0·93	0·15	0·71–1·41
		6	−0·80	0·27	0·54–1·86	−0·92	0·17	0·67–1·48
		Total		0·20	0·63–1·59		0·15	0·71–1·41
	3	1	−0·96	0·14	0·72–1·38	−0·92	0·19	0·65–1·55
		2	−0·86	0·22	0·60–1·66	−0·94	0·15	0·71–1·41
		3	−0·79	0·27	0·54–1·86	−0·94	0·17	0·67–1·48
		Total		0·22	0·60–1·66		0·17	0·67–1·48
	2	1	−0·93	0·18	0·66–1·51	−0·92	0·20	0·63–1·59
		2	−0·81	0·27	0·54–1·86	−0·93	0·17	0·67–1·48
		Total		0·23	0·59–1·70		0·18	0·66–1·51

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Examination of Table 2 reveals that in unstable cases the log A versus log χ/Q may be slightly better than log A versus log $\chi u/Q$ although the overall evaluations favor the latter. Whether this indicates some inherent differences between night and day in

TABLE 3

I Stratification parameter	II No. of classes	III Class number	IV			V		
			a′	b′	SE	a	b	SE
Unstratified	1	1	−0·55	2·12	0·25	−0·63	2·20	0·21
Lapse rate	6	1	−0·64	1·59	0·15	−0·56	2·36	0·20
		2	−0·84	0·77	0·10	−0·83	1·51	0·10
		3	−0·79	1·00	0·12	−0·70	1·90	0·17
		4	−0·95	0·56	0·13	−1·03	1·02	0·06
		5	−0·96	0·80	0·19	−1·14	0·87	0·10
		6	−0·86	1·50	0·18	−0·99	1·49	0·13
	3	1	−0·72	1·28	0·14	−0·65	2·05	0·17
		2	−0·75	1·25	0·16	−0·74	1·84	0·17
		3	−0·74	1·69	0·25	−0·98	1·42	0·16
	2	1	−0·72	1·26	0·14	−0·65	2·06	0·19
		2	−0·64	1·89	0·27	−0·91	1·55	0·17
SR	6	1	−0·62	1·64	0·12	−0·61	2·07	0·13
		2	−0·83	0·79	0·08	−0·83	1·46	0·10
		3	−0·87	0·70	0·12	−0·89	1·34	0·09
		4	−1·03	0·24	0·09	−1·04	0·99	0·06
		5	−1·09	0·38	0·13	−1·16	0·78	0·07
		6	−0·99	1·15	0·14	−1·05	1·35	0·12
	3	1	−0·69	1·37	0·13	−0·64	2·02	0·19
		2	−0·81	1·04	0·16	−0·89	1·45	0·11
		3	−0·77	1·61	0·24	−0·98	1·41	0·16
	2	1	−0·72	1·26	0·14	−0·65	2·05	0·18
		2	−0·64	1·89	0·27	−0·91	1·52	0·17
σ_a	6	1	−0·63	1·65	0·13	−0·59	2·19	0·16
		2	−0·84	0·76	0·10	−0·82	1·51	0·14
		3	−0·74	1·25	0·20	−0·83	1·50	0·13
		4	−0·77	1·32	0·23	−0·97	1·24	0·14
		5	−0·70	1·64	0·23	−0·94	1·40	0·15
		6	−0·71	1·83	0·22	−0·96	1·50	0·17
	3	1	−0·69	1·38	0·14	−0·63	2·13	0·19
		2	−0·70	1·52	0·22	−0·85	1·55	0·15
		3	−0·62	2·01	0·27	−0·90	1·58	0·17
	2	1	−0·68	1·47	0·18	−0·64	2·13	0·20
		2	−0·61	1·98	0·29	−0·88	1·61	0·17

relation to the role of wind speed (as might be the case with convection) or if it is simply

an accident of the data, remains to be seen. The fact that these relationships hold also for the higher values of σ_a may reflect the correlation of σ_a with SR in the daytime. For the Prairie Grass data a significant negative correlation coefficient between SR and σ_a was found in lapse conditions but no significant correlation in inversions.

Table 3 gives the coefficients for the various regression lines computed from the data. The formulae are

$$\log A = a' \log \chi/Q + b' \tag{3a}$$

$$\log A = a \log \chi u/Q + b \tag{3b}$$

The format of Table 3 is the same as that for Table 2 and SE is repeated for convenience.

If the slopes (a' and a) listed in Table 3 are examined some evidence of a relation between slope and stability class can be found. There is an apparent tendency for the slope to decrease (become more negative) with an increase in stability. This relationship is not absolute and is more pronounced for the log $\chi u/Q$ lines. In particular with increasing stability the SR stratification shows a decreasing slope and a decreasing intercept, except for the most stable class.

The data of Fig. 2 have been replotted in Fig. 3 but are separated by stability class. The lines are the regression lines for the six stability classes as defined by SR. Inspection of the graph reveals some overlap of stability classes but no point overlaps more than one line. The convergence of all the lines, except class 6, is clearly shown.

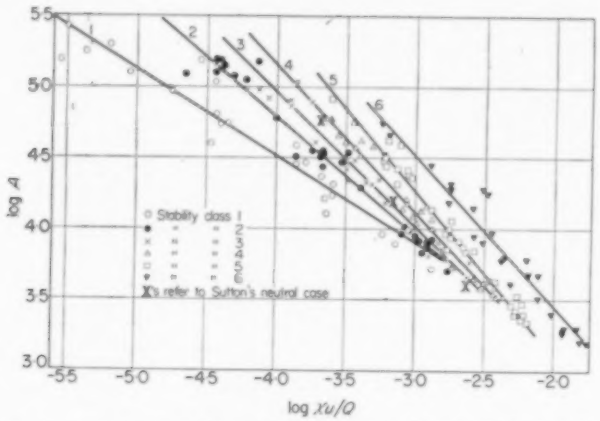

FIG. 3. Log A versus log $\chi u/Q$ showing separation by stability ratio.

The convergence of the lines implies that stability becomes less important for delineating the area when the value of relative concentration (or wind speed) increases. Since high values of relative concentration are found near the source it is probable that the cloud has not traveled long enough for stability to be important. The decrease in slope with increasing SR implies that changes in $\chi u/Q$ are more effective in changing the area in stable than in unstable conditions.

The question arises whether the regression line for stability class 6 should converge with the others or whether the divergence is real. The possibility of anomalous behavior of other micrometeorological parameters in extremely stable conditions has been noted before (e.g. BARAD and HAUGEN, 1959). It would have been possible to alter the slope of the line to agree more closely with the other lines by ignoring a few

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points. These are points where the data clearly indicate a wind direction shifting during the observation period. However, this is not *per se* a reason for discarding these runs, and the question of convergence in the most stable case must still be considered open.

The slope of the most unstable class is also subject to question. Here the areas were all of the type illustrated in Fig. 1(b) and it would not be difficult to redraw these areas or eliminate one or two runs so as to decrease the slope of the line slightly. However, *ex post facto* data decisions can become intoxicating and, as with cocktails, it can become difficult to decide when to stop once one has imbibed. Therefore no areas were adjusted after the initial drawing and no runs ignored after the initial choice.

5. COMPARISON WITH SUTTON'S FORMULA

SUTTON (1953) has presented a well-known formula for determining the concentration downwind from a continuous point source.

$$\chi = \frac{Q \exp(-y^2/C_y^2 x^{2-n})[\exp(-(z-h)^2/C_z^2 x^{2-n}) + \exp -(z+h)^2/C_z^2 x^{2-n})]}{\pi C_y C_z u^{2-n}} \qquad (4)$$

where C_y and C_z are diffusion parameters, x the distance downwind in the direction of the mean wind for the layer, u, y the cross wind distance, z the height above ground, h the height of the source and n is a parameter related to the wind profile and presumed to be a function of stability. SUTTON suggests the values

$$C_y = 0{\cdot}4 \text{ cm}^{1/8},\ C_z = 0{\cdot}2 \text{ cm}^{1/8},\ n = 0{\cdot}25$$

as being appropriate for neutral stability, (but see BARAD and HAUGEN, 1959). Equation 4 can be solved for the peak value of $\chi u/Q$ at any distance from the source and once this value has been determined the equation can be solved for the values of y at any distance between the source and the predetermined arc. In this way the x, y co-ordinates of the isopleths of $\chi u/Q$ were computed. The enclosed area was determined by plotting a sufficient number of ordinates so that a closed curve could be drawn, using the planimeter to find the area. The large crosses of Fig. 3 show the points determined in this fashion for the 800, 400 and 200 m arcs. If agreement between SUTTON's formula and the data were perfect we would expect to find the Sutton points to fall between lines 3 and 4. The 800 and 400 m points do. However the slope of the Sutton line is steeper than would be expected from the data. Nevertheless, one must conclude that the simple Sutton formula gives a good estimate of the area in the neutral case.

6. CONCLUSIONS

The above considerations resulted in a set of formulae for estimating the area within a given value of concentration divided by source strength. The inclusion of certain meteorological parameters in the simple empirical equations gave rise to a fairly reasonable range of errors. The author has concluded, on the basis of the respective scatter of points about the regression lines, that the best combination (of those tried) is given by equation 3b when the coefficients are functions of the stability class as determined by the stability ratio. This represents an improvement over the simple lapse rate and both stability parameters appear better than σ_θ, particularly in inversions.

In conclusion, the restrictions under which the formulae were derived should be stressed. The error in determining just the concentrations probably never exceeded 10 per cent. It is impossible to estimate the error in drawing the areas but it would not be surprising to find it as high as 20 per cent, particularly during lapse cases. It should also be borne in mind that the observations were made over flat uniform terrain of approximately uniform surface roughness. It is possible that the results may depend upon surface roughness and might be applicable only to the rather specialized surface type where the observations were made. Also, since data were not obtained beyond a distance of 800 m from the source, extrapolation of the results should be undertaken with caution. Whether the results can be utilized directly in other terrain features and at different distances from the source, must await further observations.

TABLE A1

Run no.	$Q(\times 10^{-3})$ (mg/sec)	u (m/sec)	800m		400m		200m		ΔT (°C)	SR °C(cm/sec)$^{\frac{1}{2}}$	σ_a (° of arc)
			χ (mg/m^3)	$A(\times 10^{-3})$ (m^2)	χ (mg/m^3)	$A(\times 10^{-3})$ (m^2)	χ (mg/m^3)	$A(\times 10^{-3})$ (m^2)			
5	77·8	5·93	0·480	126	2·82	27·2	14·8	6·81	−1·72	−0·49	9·5
6	89·5	6·80	1·12	83·9	4·24	21·9	24·2	5·69	−0·82	−0·18	M
7	89·9	4·44	0·080	272	0·760	65·1	5·14	20·8	−2·53	−1·28	25·6
8	91·1	4·52	0·725	108	4·25	23·4	26·4	5·23	−1·44	−0·70	10·2
9	92·0	7·00	0·520	156	2·90	35·0	14·2	8·41	−2·14	−0·44	10·2
10	92·1	4·68	0·175	128	2·70	29·1	11·4	9·34	−2·53	−1·16	16·8
11	95·9	7·61	1·72	57·4	7·61	15·2	29·5	4·53	−1·28	−0·22	7·2
12	99·1	7·99	1·58	72·8	5·46	21·6	20·6	5·98	−1·93	−0·30	7·9
14	49·1	1·39	21·6	33·6	146	6·21	402	1·97	3·21	16·6	3·6
15	95·5	3·22	0·535	93·7	4·78	29·3	21·7	8·01	−1·80	−1·74	12·8
16	93·0	3·31	0·080	154	0·955	39·5	6·39	13·0	−2·69	−2·46	18·5
17	56·5	3·41	9·74	29·7	26·9	9·32	86·2	2·75	0·43	0·37	5·6
18	57·6	3·22	14·0	38·7	32·3	11·6	95·0	3·36	0·80	0·77	5·3
19	101·8	6·08	0·370	123	2·30	32·4	13·4	9·35	−1·71	−0·46	11·6
20	101·2	9·38	0·795	94·3	3·42	29·1	15·9	7·26	−2·44	−0·28	8·3
21	50·9	6·11	3·26	41·3	9·03	13·0	29·6	3·85	0·32	0·09	6·6
22	48·4	7·39	2·51	31·8	8·64	10·2	27·7	3·26	0·38	0·07	5·8
23	40·9	6·05	2·09	39·9	6·36	12·6	19·5	3·86	0·19	0·08	7·3
24	41·2	5·86	1·92	45·6	5·58	14·0	17·0	4·09	0·22	0·06	7·1
25	101·4	2·75	0·235	205	1·46	55·2	8·14	16·4	−1·51	−2·00	24·8
26	97·6	6·48	0·54	156	2·75	35·2	12·9	10·3	−1·85	−0·44	13·2
27	98·8	6·13	0·98	112	4·73	29·2	19·7	7·64	−1·78	−0·47	9·2
28	41·7	2·55	10·1	43·3	21·1	14·1	59·5	4·20	0·46	0·71	6·4
29	41·5	3·94	2·60	86·7	9·18	24·6	27·6	7·06	0·94	0·61	8·0
30	98·4	6·97	0·690	120	3·02	32·7	17·5	8·06	−1·77	−0·36	10·3
31	96·0	7·87	1·67	111	4·41	30·2	17·5	8·01	−1·58	−0·26	10·9
32	41·4	2·13	58·6	19·3	121	6·21	285	2·00	1·65	3·65	3·6
33	94·7	7·56	0·74	95·8	3·95	26·7	19·1	6·43	−1·48	−0·26	10·5
34	97·4	9·20	1·30	71	5·10	21·1	20·0	5·29	−1·77	−0·21	7·3
35	38·8	1·80	13·8	47·6	76·2	9·64	253	2·03	2·57	7·93	3·3
36	40·0	1·86	38·6	21·3	64·6	8·18	203	2·60	1·12	3·53	3·8
37	40·3	4·59	2·08	59·8	7·39	15·7	22·9	4·29	0·38	0·18	7·0
38	45·4	4·28	6·44	28·0	18·7	8·89	51·4	2·92	0·50	0·27	5·0
41	39·9	3·69	9·92	23·8	25·0	6·86	67·8	2·14	0·53	0·39	
42	56·4	5·94	2·13	59·2	7·77	15·6	31·5	4·20	0·45	0·13	6·6
43	98·9	5·22	0·540	154	2·63	38·7	16·9	10·1	−2·32	−0·85	12·2
44	100·7	8·27	0·605	147	3·12	40·4	15·1	9·64	−2·19	−0·32	12·7
45	100·8	6·02	2·94	80·9	8·93	22·7	41·4	5·83	−0·58	−0·19	6·9
46	99·7	5·56	6·33	55·0	20·9	14·7	60·8	4·26	0·46	0·15	7·7
49	102·0	6·74	0·625	142	3·32	35·3	18·7	7·49	−2·36	−0·52	11·9
52	104·0	4·42	0·100	180	1·05	55·3	5·98	17·2	−2·66	−1·36	17·7
53	45·2	2·28	34·2	19·7	86·2	6·38	233	1·94	3·01	5·79	3·9
54	43·4	3·94	9·51	25·5	22·3	8·06	62·0	2·32	0·69	0·44	5·9
55	45·3	5·94	2·83	36·5	7·83	11·0	27·2	3·43	0·42	0·12	5·8
56	45·9	4·75	4·74	37·3	12·6	11·6	36·3	3·23	0·44	0·20	6·1
58	40·5	2·24	59·4	18·2	140	4·80	311	1·66	2·03	4·05	4·1
59	40·2	2·61	39·4	14·7	101	4·95	239	1·69	1·49	2·19	5·2
60	38·5	4·57	6·07	20·9	15·1	7·21	43·6	2·49	0·56	0·27	5·9
61	102·1	7·82	0·955	150	4·33	35·1	17·3	8·69	−2·20	−0·36	11·0
62	102·1	5·18	1·93	60·9	8·08	19·4	33·8	5·03	−1·09	−0·41	8·8
65	44·1	4·55	7·02	27·3	21·1	7·44	56·2	2·46	0·65	0·31	5·0
66	43·1	3·14	7·72	57·0	23·2	15·6	66·9	4·09	1·08	1·10	6·9
67	45·0	4·44	6·10	32·0	17·3	10·0	48·3	2·97	0·45	0·23	5·4
68	42·8	2·69	20·2	28·6	41·1	9·18	120	3·27	0·70	0·97	5·3

Acknowledgements—The author would like to express his gratitude to Dr. MORTON L. BARAD, Dr. MARIANO ESTOQUE and Mr. DUANE HAUGEN of the Geophysics Research Directorate for their many helpful suggestions, to Mr. ROBERT MUNZNER of Regis College and Mr. PETER ANTANAITIS of

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the Geophysics Research Directorate who aided materially with the computations, to Mr. ROGER LANDERS of the Geophysics Research Directorate, who prepared the illustrations, and to Miss MARGO SYLVESTER and Miss HELEN SCOTT of Regis College who helped prepare the manuscript.

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APPENDIX

Table A1 gives the basic data from which the regression lines were computed. The source strength Q is given in the first column, the 2-m wind speed in the second. The values of peak concentration χ and the corresponding values of the area A for the three arc distances are given in the succeeding columns. The last three columns give the temperature difference ΔT between the 4 m level and the $\frac{1}{2}$ m level, the stability ratio SR as given by equation 2, and the standard deviation of the azimuth angle of the wind σ_θ.

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Int. J. Air Poll. Pergamon Press 1959. Vol. 2, pp. 127–131. Printed in Great Britain.

NOTE ON THE EXCHANGE OF IODINE BETWEEN THE ATMOSPHERE, LAND AND SEA

BERT BOLIN
International Meteorological Institute, Stockholm
(*Received* 11 *May* 1959)

Abstract—The deposition of ^{131}I as observed in small scale experiments and also after the Windscale incident, are interpreted in the light of available measurements of ^{127}I in the atmosphere and in plants. It is shown that the deposition velocity deduced from deposition of radio-iodine is representative of the gross transfer while the net flux from the atmosphere to a land surface is several orders of magnitude smaller. The observations show that plants use atmospheric iodine for their assimilation and that this may be their major source in spite of the indication that a larger portion of the atmospheric iodine is present in organic form and not readily available for assimilation. Finally a residence time of 20 days for iodine in plants is deduced.

1. INTRODUCTION

THE exchange of iodine between the atmosphere and the earth's surface has acquired renewed interest because of the presence of radio-iodine, ^{131}I, in the debris spread from atomic bomb explosions and particularly because it is most likely to be a major constituent of the radioactivity released in atomic energy plant accidents as, for example, was the case at Windscale in October 1957. With this in mind CHAMBERLAIN and CHADWICK (1953) have carried out experiments to determine the rate of deposition of radio-iodine on vegetation. Extensive measurements made after the Windscale accident are also available (STEWART and CROOKS, 1958; CHAMBERLAIN and DUNSTER 1958; DUNSTER *et al.*, 1958; BOOKER, 1958). There are, however, some facts in the data reported that have not received a satisfactory explanation and, as we shall see, actually give interesting information about the processes of exchange of iodine between the air and the underlying surface. It is particularly important to look at these recent measurements in the light of earlier observations of inactive iodine (mainly ^{127}I) in the air, precipitation, vegetation, rivers and the sea. A large number of such measurements exist, especially through the work of VON FELLENBERG (1926) and CAUER (1933) and also a number of more recent investigators. The present note is intended to point out a few important aspects of the exchange processes at work and to indicate the need for further investigations.

2. THE EXCHANGE OF IODINE BETWEEN THE ATMOSPHERE AND A LAND SURFACE AS DEDUCED FROM ^{127}I MEASUREMENTS

The amounts of iodine found in the atmosphere vary considerably. Maximum values over the sea may be as high as 10 $\mu g/m^3$, while hardly detectable quantities of iodine are found in some areas far from the oceans. Obviously transport of iodine from the sea to land areas takes place through the atmosphere and at least part of the iodine deposited on land originates from the sea. This process is similar to that of chloride investigated by ERIKSSON (1955). Since presumably no significant accumulation occurs over land this inflow has to be balanced by an outflow through the rivers.

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VON FELLENBERG (1926) reports a few measurements of iodine in river waters in Switzerland giving values of 0·4–1·3 μg/l. Recent Swedish measurements on surface waters by SJÖSTRÖM (1956) support these observations. The iodine concentrations found in precipitation are about the same (values up to about 4 μg/l). Since the water run-off by rivers is only a fraction of the total precipitation *no appreciable net dry deposition of iodine from the atmosphere* on vegetation and the soil occurs. It is for example easily estimated that if an air concentration of about 0·5 μg/m^3 is assumed and a total run-off of about 40 cm of water/year takes place, the deposition velocity for *net* transfer of iodine can hardly exceed 0·01 cm/sec and may even be negative. Of course the gross transport to and from the ground may be and most likely is much greater. (Deposition velocity is defined as the ratio of the average amount of isotope deposited per unit area and unit time to the mean concentration of isotope in the air.) This should be compared with the deposition velocities of about 2·5 cm/sec which CHAMBERLAIN and CHADWICK (1953) obtained in their field experiment using radio-iodine.

If we assume that this latter deposition velocity applies to the natural iodine in the air, we find ourselves led to quite impossible conclusions about the amount of iodine which should be present in vegetation. Obviously most of the iodine deposited on vegetation and partly used by the plants is later returned to the atmosphere. VON FELLENBERG (1926) also reports extensive direct measurements of such a release from the soil. In view of the fact that iodine is volatile at ordinary temperatures it is possible that some of it is returned to the atmosphere quite soon after absorption, i.e. directly from the leaves of the plants. It is in any case of interest to see how long a time is required to deposit the iodine present in the plants at any time. A deposition velocity of 2·5 cm sec^{-1} as measured by CHAMBERLAIN and CHADWICK (1953) would for example mean an accumulation of about 10 μg/cm^2 over a 100 day period. (An air concentration of 0·5 μg^{127}I/m^3 has been assumed and 100 days may be taken as the characteristic time of growth for grass and similar plants.) VON FELLENBERG's measurements of iodine in plants gave values of about 50 μg/kg. Assuming a plant mass of about 0·1 g/cm^2 (which still is more than in the cases studied by CHAMBERLAIN and CHADWICK) means that there will be a total amount of 0·005 μg/cm^2 of iodine in a grass field. This is several orders of magnitude less than would result from deposition with a velocity of 2·5 cm/sec. As a matter of fact, the amount present in grass would be deposited in about 1 hr with this rate of deposition.

The exchange of iodine between the atmosphere and a land surface seems in some respects to be similar to ordinary condensation and evaporation. Molecules pass from the atmosphere to the plants and the soil but also return to the atmosphere resulting in a *net* transfer that is usually several orders of magnitude less than the gross transfer in any direction. The iodine present in living plants and also on their surface may return to the atmosphere directly or via the soil after having been washed down by precipitation or transferred by the plant and its root system. Very little is known about this transfer and further investigations are desirable. However, recent measurements of ^{131}I shed some light on the character of these exchange processes and we shall be able to resolve the dilemma indicated above.

3. DEPOSITION OF RADIO-IODINE

The measurements of deposition of radio-iodine should be interpreted in view of the

general ideas indicated above. Conditions in the field experiment reported by CHAMBERLAIN and CHADWICK (1953) and after the Windscale accident were, however, quite different. In the former case (hereafter denoted as case I) radio-iodine was released for 20 min resulting in atotal maximum dosage of about 100 $\mu\mu c\ sec^{-1}\ cm^{-3}$ at the points downstream, where measurements were made. The average deposition velocity as defined above was about 2·5 cm sec^{-1}. At the Windscale accident (here denoted as case II) the release lasted for about 24 hr with a total dosage at nearby places very much higher, but at distant places considerably lower than in case I. Simultaneous measurements of air concentration and deposition are available only in a few cases at about 100 km distance from the place of release. Deposition velocities of 0·2–0·5 cm sec^{-1} were here obtained.

In case I the activity in the grass rose from 0 to about 250 $\mu\mu c/cm^2$ in areas of maximum deposition, where the average air concentration had been about 0·1 $\mu\mu c/cm^3$. Using the same concentration of ^{127}I in the air and vegetation as quoted before means that the relative concentration in the grass had risen to about 0·05 $c^{131}I/g^{127}I$ while the air on an average contained about 0·2 $c^{131}I/g^{127}I$. Of course the amounts of ^{127}I are quite uncertain, since no direct measurements were made, but they are most likely of the correct order of magnitude. Similar estimates in case II are somewhat more difficult due to highly varying conditions and incomplete observations. At Harrow, Middlesex the first iodine in the air was observed on 11 October, around 4 p.m. Maximum concentration of about 0·001 $\mu\mu c/cm^3$ was reached 10 hr later and at noon the following day the iodine cloud had essentially passed (see STEWART and CROOKS, 1958). The total deposition on grass amounted to about 5 $\mu\mu c/cm^2$ (as can be estimated from the figures presented by BOOKER (1958). In the same way as before we estimate the $^{131}I/^{127}I$ ratio in the air at the time of maximum concentration to be about 0·002 $c^{131}I/g^{127}I$ and 0·001 $c^{131}I/g^{127}I$ is obtained for the grass. We notice thus that the $^{131}I/^{127}I$ ratio in the plants probably did not exceed that of the air until after the maximum concentration in the air had been reached and thus about 10 hr after the beginning of the radio-iodine exposure. These results in deposition velocities are about one order of magnitude less in case II than in case I.

It is tempting to conclude that an equilibrium state is reached when the $^{131}I/^{127}I$ ratios become the same in the air and in the plants. There are, however, several observations that indicate that this probably is not the case:

(a) The observation that such a state thus should be reached after 1 (or a few) hour(-s) would imply a very rapid adjustment towards a new equilibrium and that the residence time for iodine in plants would also be of the order of hours, which seems rather unlikely for physiological reasons.

(b) One would in such a case also expect a rapid adjustment towards a small $^{131}I/^{127}I$ ratio, when the corresponding ratio in the air fell to values close to zero soon after the maximum concentrations were observed. This did not happen in case I nor in case II. In the former case no significant " evaporation " of iodine from the grass was measured and the same thing is obvious in case II from the fact that the ground γ-radiation decreased with time with a " half-life " close to 8 days, which is the radioactive decay time for ^{131}I (cf DUNSTER *et al.*, 1958).

In view of what has been said above it would be of considerable interest to repeat the measurements made by CHAMBERLAIN and CHADWICK (1953) but extending the

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experiment over several hours or a full day, making simultaneous measurements of the ^{127}I concentrations and possibly also controlling the ^{127}I content of the air.

A more careful study of already existing measurements reveals another explanation, that seems more likely than the assumption of an exceedingly short residence time of iodine in plants. The radio-iodine released in case I as well as in case II was in free form and thus directly available to the plants. Recent measurements of ^{127}I in the atmosphere indicate on the other hand, that by far the greater part is present in *organic* form (SVENSSON and ERIKSSON, 1959). In estimating the residence time for iodine in plants from the change of the $^{131}I/^{127}I$ ratio in the plants to that of the atmosphere, one should therefore only consider the part of the iodine in the air that can be readily assimilated. The proper value of this ratio in the air would therefore be considerably greater than that in the plants both in case I and case II and conditions were all the time far from equilibrium.

Some other measurements in case II permit us to estimate the likely residence time of iodine in plants (grass) which more closely agrees with our ideas about the rate of the assimilation process. This also indirectly supports the idea put forward above. Repeated measurements of ^{131}I in grass and milk were carried out after the Windscale incident (cf BOOKER, 1958). A regular decrease of the radio-iodine concentration with an apparent half-life of about 5 days was observed in both the grass and in milk. It is first of all interesting to note that the almost identical values obtained for grass and milk are in agreement with the rate of the iodine metabolism in cows as we know it from experiments carried out by LENGEMANN and SWANSON (1957). They have shown that the residence time of iodine in the animal is only about 2 days. It is then easily shown that within less than a week, during which an adjustment takes place, a regular decrease of the ^{131}I content of the food should be associated with a similar decrease of the ^{131}I content of the milk with very similar apparent decay times. Remembering now that the radioactive decay time (λ) of ^{131}I is 8 days and denoting the apparent half-life for radioactivity in the grass by σ we obtain the mean life time (κ = residence time) for an iodine molecule in the grass from the equation

$$\frac{\ln 2}{\kappa} = \frac{1}{\sigma} - \frac{1}{\lambda}$$

With the values for σ and λ given above $\kappa \approx 20$ days. Since presumably the iodine in the atmosphere is in approximate equilibrium with the iodine in the plants, it would mean that some 5 per cent of the iodine in a plant is replaced each day from the atmosphere. This is 10–100 times slower than the one indicated from the rate of deposition of ^{131}I as shown above and would mean that only a few per cent of the iodine in the air can be used by the plants. The implication that there is a selection in the iodine deposition on plants also suggests that the plant is actively assimilating only certain forms of the iodine. As was pointed out before, however, the necessary amounts of iodine can easily be supplied from the atmosphere. It would be interesting to make direct measurements and to try to verify these conclusions.

Quite different deposition velocities were found in case I and case II. One may think of several reasons for this. The turbulent transfer through the atmosphere might have been considerably lower in the second case on account of stable stratification. A deposition velocity of 1·7 cm/sec had, however, been obtained in case I in a night-time experiment with light winds. Another explanation may be that plant assimilation of iodine is much less in the fall. It is of some interest to note, however, that a

similar effect might also be expected if a gradual transfer occurs in the atmosphere of pure iodine into more complex compounds, which are not immediately available for assimilation.

The apparent decay time of 5 days for radio-iodine in the grass is due to a gradual transfer into the soil (BOOKER, 1958), which presumably takes place through the roots. It was previously indicated that the net transfer of ^{127}I from the atmosphere to a land area is quite small and thus about as much iodine must return to the atmosphere as is brought down into the soil. Due to the large amounts of iodine present in the soil in comparison with the amounts transferred, the residence time of an iodine molecule is quite large as compared with the decay time of radio-iodine. It is therefore quite unlikely that any appreciable amount of the radio-iodine is returned into the atmosphere before it decays radioactively.

Acknowledgement—The author is particularly indebted to Dr. E. ERIKSSON for many helpful discussions.

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MEASUREMENTS ON THE CONTENT OF NON-VOLATILE ORGANIC MATERIAL IN ATMOSPHERIC PRECIPITATION

GEORG HUGO NEUMANN*, STIG FONSELIUS and LARS WAHLMAN
International Meteorological Institute, Stockholm
(*Received* 27 *May* 1959)

Abstract—A method is described for the determination of the non-volatile organic carbon and the total nitrogen content in atmospheric precipitation.

The fall-out of organic carbon was measured at nine stations in Sweden over a period of 4 months for one test series. Geographically the distribution of organic carbon was found to be fairly constant over the total sampling region averaging 160 mg carbon per square meter per month.

In a second test series the ratio organic carbon to total nitrogen (ammonia + organic nitrogen) was also determined. This too was found to be fairly constant irrespective of the sampling place.

It is concluded that the organic carbon in the atmosphere has a very extended source region. It is further suggested that the sea surface might play an important role as a provider of organic material found in the atmosphere.

INTRODUCTION

DURING the past decades several investigations have been reported on the content of inorganic material in atmospheric precipitation. A rather complete bibliography has been worked out by ERIKSSON (1952). From this bibliography it is seen that much work has been carried out in determining various constituents such as alkali metals, magnesium, calcium, ammonia, sulphur, nitrate and chloride, whereas the content of organic material has received only limited attention. The reason for this might have been partly the obvious analytical difficulties involved in determining the very low concentrations of organic matter in precipitation, and partly that the geochemical and agricultural interest have hitherto mainly been centred around the mineral constituents.

However, a few investigators have reported determinations of organic matter in rain and snow. For instance SHUTT (1909–1924) has published several extended series of determinations including " albuminoid " nitrogen. These determinations consisted mainly of the liberation of organically bound nitrogen by distillation with an excess of alkaline permanganate solution. However, this method involved only part of the organic nitrogen and gives little information about the total amount of nitrogen present in the sample. Among the more recent investigations the one of VIRO (1953) should be mentioned. He determined the loss of weight by ignition of the solid evaporation residues of his samples. In this way VIRO found an average content of about 50 per cent organic material in the solid residues. These determinations require however big samples and they provide a rather crude estimation of the average content of organic material.

Very little has been written about the regional distribution and the qualitative nature

* Present address: Nobel Institute of Physics, Stockholm.

of the organic substances in precipitation. Some amino acids have been reported by FONSELIUS (1954).

The authors therefore have carried out an investigation on the content of organic carbon and nitrogen in rain and snow samples from different places in Sweden. It may be pointed out, that in this paper, the nitrate and nitrite nitrogen are excluded. " Organic N " means the nitrogen which is distilled as ammonia in the Kjeldahl procedure, reduced with the free ammonia estimated by NaOH distillation. " Total N " means free ammonia N + organic N.

SAMPLING AND PREPARATION FOR ANALYSIS

In the Scandinavian network for the chemical examination of air and precipitation (EGNÉR and ERIKSSON, 1955) nine of the stations have been equipped with an extra glass funnel for sampling of precipitation for organic analysis (Fig. 4). The precipitation was collected in 500 ml Jena glass bottles containing 25 ml of 0·4 M hydrochloric acid to inhibit biological activity in the samples. This will give the final sample a pH below 1·7. LOHAMMAR (1938) has shown that among a number of fixation means (toluene, mercury salts, NaOH and HCl) HCl was the best one. According to SKINNER *et al.* (1949) only very few micro-organisms may be active in an acid medium below pH 2.

Monthly samples were analysed at the International Meteorological Institute in Stockholm. The glass funnels used in the sampling of precipitation have an area of 63 cm². This gives 315 ml of water per 50 mm of precipitation. The composition of these samples can be compared with the corresponding chemical data obtained from the ordinary Scandinavian network (EGNÉR and ERIKSSON, 1955), providing that differences in evaporation from the ordinary and the extra sample collector are negligible. Experiments showed that the ratio between the amounts of precipitation collected in both funnels did agree in fact with the ratio between the areas of the funnels within a few per cent.

Occasionally samples were also collected from snowfalls at places far removed from any local source of pollution. As these samples were analysed within a few days after the collection, no hydrochloric acid was needed to ensure the absence of biological activity.

In the laboratory the samples were immediately filtered through a sintered glass filter (Jena G3). The samples were stored at +4°C in a dark room. Previous to analysis approximately 20 mg sodium chloride and 1·5 ml concentrated orthophosphoric acid were added per liter of the sample. Another 60 ml was spared in a separate bottle for later estimation of total sodium (inclusively the extra sodium).

EVAPORATION

The samples were evaporated using a vacuum-distillation apparatus equipped with an arrangement for continuous evaporation (Fig. 1). The apparatus consists of a Claisen flask with a conical bottom. In the neck *A* a glass tube *B*, containing a capillary tube *C*, is inserted. A side tube *D* is connected with the sample container *E* The flow of liquid is regulated with the screw clamp *F*. The capillary tube *C* and the sample container *E* are equipped with quartz-wool filters moistened with concentrated phosphoric acid to protect the sample from possible ammonia in the laboratory air. The vacuum employed varied between 15 and 25 mm Hg, which kept the equilibrium

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temperature in the evaporation vessel safely below 40°C. The yellowish residue (1–2 ml) from the evaporation is gathered in the bottom of the distillation vessel. This residue is free from carbon dioxide and chloride (FORSBLAD, 1955).

The phosphoric acid renders the residue highly viscous permitting the withdrawal of three aliquots which are homogeneous with respect to carbon, nitrogen and

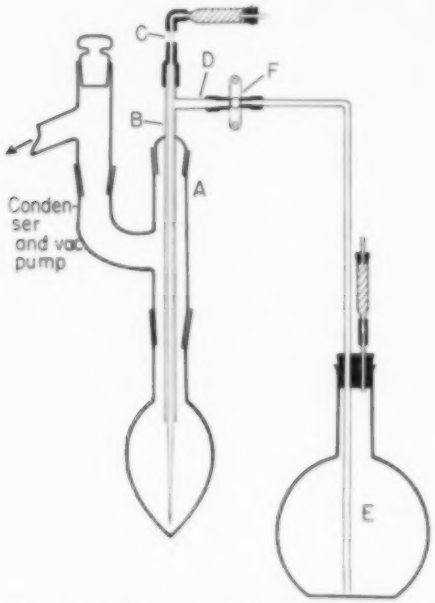

FIG. 1. The evaporation apparatus for continuous evaporation.

sodium. The aliquots were then used in the procedures (a), (b) and (c) (described later).

In this paper only the content of non-volatile organic matter in the precipitation has been determined. However the amount of volatile organic material present, is probably very small. In order to get a rough estimation of " medium " volatile organic matter soluble in *n*-hexane, the distillate from an average sample was extracted with *n*-hexane and the dry residue was determined. No measurable amount of such organic matter was found.

ANALYSES

(a) *Wet Combustion of Organic Carbon* (Fig. 2)

One aliquot is introduced into the small combustion vessel *G* (bulb volume 10 ml) and is dried in an airstream at 60°C to remove most of the water present. Otherwise the combustion may be incomplete for some constituents. A few small porcelain pieces and around 100 mg of solid potassium iodate are added. The vessel *G* is tightly attached to the reflux condenser *M* with laboratory clips. A few drops of the combustion liquid (or concentrated phosphoric acid) are used for lubrication of the ground joints, which were previously completely dried to maintain the viscosity of the

lubrication. In about a hundred experiments only one case of gas leakage through this joint occurred due to overpressure in *G-M*.

The taps *B*, *H* and *K* are opened and CO_2-free N_2 is introduced into the apparatus in a vigorous stream via *A* in order to drive out CO_2 present in the combustion and absorption units. While CO_2-free N_2 is still passing through the apparatus, 10 ml of

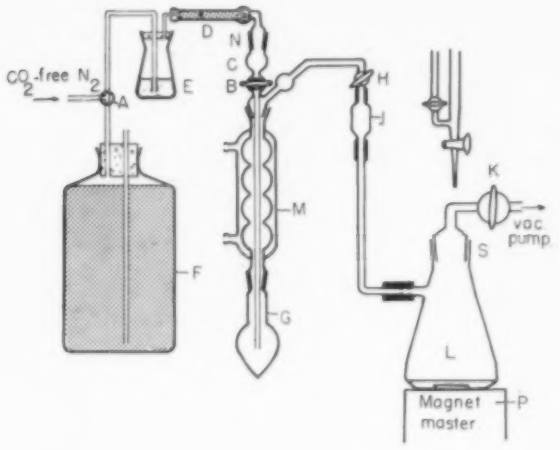

FIG. 2. The apparatus for wet combustion of organic carbon.

the absorption solution are introduced into the Erlenmeyer flask *L* (250 ml volume). The vessel *L* is closed through the joint *S* (*K* open). The gas stream is stopped, *B* is closed and the system is now immediately evacuated. *K* and *H* are closed. The joint *N* is disconnected while a slow gas stream (CO_2-free N_2) is passing the bubble counter *E* and the filter *D*, and 3 ml of the combustion liquid are delivered to the vessel *C*. The slow gas stream through *E* is stopped, the joint *N* is connected and the tap *A* is opened to *F*. Now the tap *B* is slowly turned to allow the combustion liquid to be sucked down into *G* through the narrow glass tube in the centre of the reflux condenser *M*. The rest of the vacuum in the combustion unit is filled up with CO_2-free air from the reservoir *F* (two-thirds filled with soda lime). *B* is closed and the bulb of *G* is heated with a micro burner. The combustion liquid will rapidly evolve oxygen, which causes a foam collar in the neck of *G*. After a few minutes the combustion liquid turns green and later dark. The heating is stopped when violet iodine vapours begin to escape. This formation of iodine vapour has been observed to be a good indicator of complete combustion. In the case when too much water is present in the sample introduced in *G*, iodine vapour fails to appear.

The vessel *G* is allowed to cool for some time and is later further cooled in water. After about 5 min almost all gaseous SO_2 and I_2 left in the combustion unit is condensed and the SO_3-mist formed during the combustion has largely settled. Now the tap *H* is carefully opened in order to let the gas from the combustion unit slowly enter the absorption vessel *L* via the filter *J* which is filled with Devardas alloy which proved to be an excellent absorber for I_2 and SO_3 vapors. The magnetic stirrer is started and a moderate flow of CO_2-free air is allowed to pass from the reservoir *F* through the

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central tube of *M* to the absorption vessel *L*. The airstream is regulated with the tap *B* and after about 5 min the vacuum in *L* should be filled up. The narrow passages between the four bulbs and the narrow central tube of the reflux condenser will maintain a quasi-laminar flow of CO_2-free air from *G–M* to *L*. Experiments with this arrangement showed that about 200 ml (n.t.p.) of CO_2-free air were needed in order to remove 99 per cent of the CO_2 present in the combustion unit (*G–M*), the volume of which is 60 ml. After 10 min the absorption is complete. Then a vigorous stream of CO_2-free N_2 is passed through the entire system. When a slight over-pressure is reached the stopper *S* is removed and a few drops of the indicator are added. The content of the absorption vessel is titrated with 0·03 M standardized HCl, using a 10 ml burette graded in 1/20 ml.

In order to make a correction for possible organic material in the combustion liquid and for various titration errors, two blanks are run. The allowable tolerance was that the values could not differ more than 0·02 ml from each other.

The total amount of carbon in milligrams introduced in *G* is equal to

$$6(b - a)m$$

where b = ml of HCl consumed in a blank determination
a = ml of HCl consumed in the analysis
m = molarity of the HCl used in the titration.

Reagents for wet combustion

Combustion liquid : 1·5 g KIO_3, 15 g CrO_3, 30 g P_2O_5, 130 ml conc. H_2SO_4 and 25 ml 90% H_3PO_4 (all reagent grade) are mixed in the mentioned order and the mixture is heated to 160°C for a few minutes. After cooling it is kept in a glass-stoppered flask and protected against dust, since dust would reduce the oxidizing power of the solution. Such a solution should not be kept more than a few weeks.

Potassium iodate : reagent grade (carbon-free).

Absorption solution : 10 liters contain 29 g $Ba(OH)_2$ and 50 g $BaCl_2$ (according to FONSELIUS *et al.*, 1955).

Hydrochloric acid : 0·03 M prepared by dilution of standardized 0·1 M acid.

Indicators : 0·1% Cresolphthalein, alcoholic solution.

Analysis of standard samples

In order to test the performance of the wet combustion method the following samples of succinic acid were analysed. The solution contained 1·000 mg of carbon per ml. Previous to combustion 0·1 ml of conc. orthophosphoric acid was added to each sample in *G* and the sample was dried.

Carbon introduced (μg)	Carbon found (μg)
288	281
288	275
288	290

It was not found necessary to make further tests on different organic substances as the combustion mixture has previously been tested on a number of different substances (ARCHER, 1954).

Analysis of the orthophosphoric acid used in the determinations

The analyses were carried out on two samples of orthophosphoric acid (Merck, " Acidum orthophosphoricum 1·70 "). It was found that the content of carbon and nitrogen (Kjeldahl) was less than 10 μg/ml.

(b) *Micro Kjeldahl Determination* (Fig. 3)

The second aliquot of the residue is transferred to a Pyrex test tube (150 × 15 mm). From a burette 0·2 ml of digestion mixture (40 g K_2SO_4, 2 g selenium reaction mixture, 250 ml conc. H_2SO_4 and 250 ml distillated water) is added and the tubes are heated

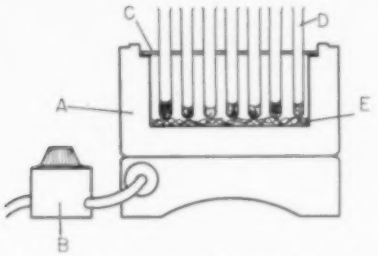

FIG. 3. The furnace for Kjeldahl digestion.

to 300°C in a furnace *A* equipped with an energy regulator *B* and covered with an asbestos shield *C* with holes for the test tubes *D*. The bottom of the furnace is equipped with an iron net *E*, which prevents the tubes from direct contact with the furnace. In 4 hr the digestion is finished, and the tubes are removed and allowed to cool. The residue is diluted with ammonia-free redistilled water, transferred to 100 ml distillation vessels, which are filled up to 50 ml with redistilled water and the ammonia content is determined by distillation with NaOH according to EGNÉR *et al.* (1955).

In this connexion the free ammonia content is determined using 50 ml of the original sample which has been spared for this purpose.

(c) *Determination of Sodium*

The last aliquot is diluted to 25 ml and analysed for sodium with a flame photometer. An Eel model A equipped with a 50,000 Ω potentiometer was used. Finally the concentration of total sodium (originally present in the sample + extra) is determined in the same way.

CALCULATIONS

From these three analyses and from the volumes of the different aliquots we obtain the total amounts of sodium, carbon and nitrogen present in a unit volume (e.g. 1 ml) of the residue from evaporation.

For example assume these amounts to be designated as follows

s = mg Na/ml residue

c = mg C/ml residue

n = mg N/ml residue.

From the original concentration of the total sodium in the sample before evaporation (t mg/l) we obtain

$$\text{total carbon concentration} = \frac{c}{s} \times t \text{ mg/l}$$

$$\text{total nitrogen concentration} = \frac{n}{s} \times t \text{ mg/l}.$$

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A main advantage of the method described is the possibility of determining carbon simultaneously with nitrogen or any other constituent in one single evaporation, thereby minimizing large evaporation and transference errors. The precision of the method is, however, limited by the moderate accuracy of the sodium determinations.

The reproducibility of the analyses is illustrated by the following series of determinations (Test sample: snow collected near Stockholm, February 1959)

	C(mg/l)	N(mg/l)
	2·7	0·54
	2·6	0·51
	2·5	0·52
	2·5	0·51
	2·8	0·53
	2·5	0·51
	2·7	0·51
Average	2·6	0·52

The average deviation from the mean value is less than 5 per cent in both determinations. The ratio C/N equals 5·0.

RESULTS AND DISCUSSION

TABLE I. AVERAGE CONTENT OF ORGANIC CARBON AND INORGANIC MATTER IN PRECIPITATION FOR THE PERIOD MAY–AUGUST 1958 (The stations are found on Fig. 4)

Station	Carbon (mg/l month) (average)	Carbon (mg/m² month) (average)	Inorganic matter (mg/m² month) (calculated average)	Ratio carbon: inorganic matter
Ar	2·5	130	149	0·87
Fl	1·7	170	227	0·75
Fi	2·7	160	543	0·30
Pl	2·4	150	527	0·28
Rä	3·4	180	179	1·00
Rö	2·5	160	155	1·03
Sm	3·1	200	297	0·74
Ul	1·9	160	243	0·66
Åh	2·5	120	184	0·65
Mean value	2·52	160		

In Table 1 and Fig. 4 the data are given for those Scandinavian network stations which were equipped with extra funnels. It is seen that the average monthly fall-out of organic carbon per square meter is fairly constant for all stations, the mean value being 160 mg. Assuming the organic matter to contain about 50 per cent carbon this gives an annual fall-out of about 4 g organic matter per square meter. This is in fair agreement with VIRO's value of 2·74 g obtained from Finnish samples.

From the values of inorganic matter listed in Table 1, we find that the ratio of organic matter to inorganic matter increases from 0·6 at the coast (Fi) to about 2·0 at a typical inland station (Rö). Data for nitrogen are not given in Table 1 as it was

FIG. 4. The network for organic samples.
The crosses indicate the areas where the snow samples were taken, 1. Edsviken, 2. Dalecarlia, 3. Åre.

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TABLE 2. CONTENT OF CARBON AND NITROGEN IN SNOW SAMPLES

Sample	C (mg/l)	$N_{tot.}$ (mg/l)	NH_3–N (mg/l)	$C/N_{tot.}$
D_8	1·9	0·41	0·45	4·6
D_{15}	1·2	0·35	0·24	3·4
D_{17}	1·4	0·35	0·18	4·0
D_{20}	1·1	0·26	0·25	4·3
D_{25}	0·8	0·20	0·07	4·0
Åre	0·8	0·25	0·06	3·3
6 April 1958				
Bredkälen	1·2	0·20	0·05	6·1
3–4 January 1959				
Edsviken	1·5	0·39	0·20	3·9
12 December 1958				
Edsviken	1·9	0·40	0·05	4·6
10 January 1959				
Average	1·3	0·31		4·3

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found that the content of ammonia in the samples was abnormally high, frequently amounting to more than 1 mg NH_3–N per liter. It is believed that the extra HCl added for preservation against biological activity highly served to increase the absorption of gaseous ammonia from the surrounding air.*

In Table 2 the concentrations of carbon, total nitrogen (Kjeldahl) and " free " ammonia (distilled with NaOH) are given for a number of snow samples. The samples marked " Edsviken " were taken at a place about 10 km outside Stockholm. All other samples were taken at different places in an unpopulated forest region in the middle part of Sweden. Thus samples marked " D " are from an area of 10 000 km² in north-western Dalecarlia, and the samples " Bredkälen " and " Åre " are from a region about 200 km more to the north (see Fig. 4).

It is seen from Table 2 that the " free " ammonia constitutes between 25 and 100 per cent of the Kjeldahl nitrogen possibly indicating a varying degree of decomposition of organic matter in the samples. Assuming most of the nitrogen to be of organic origin, it is found that for the composition of organic matter, the ratio carbon to nitrogen is fairly constant. The average is 4·3 : 1. It is reasonable to assume that most organic nitrogen covered by the Kjeldahl procedure originates from proteins. This would tentatively mean a content of

proteins (50%C, 16%N)	about 70%
other organic species	about 30%

* Note: Analyses for inorganic matter are reported in the current data from the Scandinavian network (*Tellus* **10** (1958), **11** (1959)). S is counted as SO_4, NO_3–N as NO_3 and NH_3–N as NH_3.

The limited number of observations does not permit more general conclusions. However, the fairly uniform composition and distribution of the samples seems to indicate that the organic matter in the atmosphere has a very extended source region. It seems quite possible that the organic matter present on large areas of the sea as a surface film (KIENTZLER *et al.*, 1954) could be transported into the air by a bubble spray mechanism. In this process there is formed a broad spectrum of small droplets of which the bigger ones seem to be responsible for most of the salt transport from the sea surface. Minute droplets from the rupture of the surface film of the bubbles (MASON, 1954) are formed together with these bigger droplets. These minute particles carry most of the organic matter from the surface film and, being less hygroscopic than the bigger salt nuclei, would have a longer residence time in the atmosphere. This mechanism could explain the uniform distribution of organic matter per unit area and even explain the increasing ratio organic matter to inorganic matter towards inland. The sea has often been suggested as a source for ammonia in the atmosphere. It has been assumed that this ammonia is produced by decomposition of organic nitrogen compounds in the water. The main difficulty in substantiating such theories has arisen from the fact that the conditions in the sea water and the properties of ammonia do not favour an escape of free ammonia. However, a more plausible explanation for the exchange of ammonia nitrogen between the sea and atmosphere can be given by assuming the organic matter to first *be transported up in the air and then to be decomposed to ammonia.*

Acknowledgements—We wish to express our gratitude to Professor H. EGNÉR of the Royal Agricultural College in Upsala for the installation of the funnels and for the sampling work. The investigation has been supported by grants from Statens Naturvetenskapliga Forskningsråd (National Research Council).

LT. COL. DONALD E. MARTIN has corrected the translation into English and made a number of valuable suggestions regarding the language.

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METHODS OF SAMPLING AND STORAGE OF AIR CONTAINING VAPORS AND GASES

ROBERT A. BAKER and ROBERT C. DOERR
The Franklin Institute
Laboratories for Research and Development
Philadelphia 3, Pennsylvania
(*Received* 15 *May* 1959)

Abstract—This study was made to determine the effect of various storage techniques and materials on known concentrations of gases in air. These gases were studied as single components and as complex mixtures under atmospheric and compression storage conditions. Storage was in steel cylinders, plastic bags and glass flasks at varying time intervals. Results were monitored by infrared spectrometry and by gas chromatographic procedures.

Compression storage in steel cylinders at 150 psig resulted in high loss of sulfur dioxide and nitrogen dioxide but little hydrocarbon loss. The compressor was found to affect the mineral oxides, especially sulfur dioxide. This technique appears satisfactory for hydrocarbons.

Various polymeric films were fabricated into bags and evaluated as gas storage containers at atmospheric pressure. Moisture, regardless of whether present originally or having permeated into the bag on storage, was a major factor. Mineral oxides disappearance is more rapid at high relative humidity. Hydrocarbons were not similarly influenced. Chemical reaction and permeability are involved with the soluble mineral oxides but diffusional parameters alone control hydrocarbon loss. These statements apply only if the gases are nonreactive with the plastics.

Two-film bags may be useful in field testing. The inner film should be impermeable to the gases of interest and the outer film to moisture. Aluminized Mylar was the least permeable to moisture of the plastic films studied. Additional study under conditions of controlled humidity are contemplated to define comparative performance of the films.

Gas–liquid chromatography and plastic bags offer potential benefits in field testing of air pollution. Small volumes at low concentrations may be accurately measured if the specific analytical procedure is available.

The occurrence of a dark reaction could not be demonstrated after 46 hr storage of a mixture of sulfur dioxide, nitrogen dioxide and 2-pentene. Measurement was by light scattering.

Storage of the sulfur dioxide, nitrogen dioxide, 2-pentene mixture in steel cylinders at atmospheric pressure showed no significant loss. Comparable storage in glass flasks showed high loss of sulfur and nitrogen dioxides.

INTRODUCTION

THE object of this study was to determine the effect of various storage techniques and materials on known concentrations of gases in air. These gases were studied as single components and as complex mixtures under atmospheric and compression storage conditions. Storage was in steel cylinders, plastic bags and glass flasks at varying time intervals. Results were monitored by infrared spectrometry and by gas chromatographic procedures.

Recent developments in the field of air pollution have necessitated the detection and identification of very small concentrations of specific gaseous components in the atmosphere. The analytical equipment, such as the long-path infrared spectrometer used to measure small concentrations, requires large volumes of sample. The com-

plexity of the analytical instrumentation prevents field analyses. In order for analysis to be made with reliability, it is necessary that gaseous samples obtained in the field be transferred to the laboratory without change in concentration or composition.

Plastic film bags are logical choices as air sampling containers. They are light, easy to handle, and expand or contract with changes in gas volume. Permeability of gases and vapors through polymeric films has been studied by various investigators. Certain basic relationships have been established and specific applications examined. BRUBAKER (1953) found the log of permeability to be a linear function of the reciprocal of temperature. The mechanism of diffusion was discussed by SIMRIL (1950) who noted that introduction of side chains into the main polymer, plasticizers and water increase permeability. MEYER (1957) found no differentiation of permeability constants of pure gases and mixtures. Gas does not affect water vapor transmission although water vapor affected gas transmission through hydrophilic films. CROWE (1957) presented a kinetic theory to account for both ordinary and thermal diffusion of gas through polymeric films. GARNER (1956) showed that HNO_3 permeability was restricted to a limited number of surface sites for polychlorotrifluoroethylene films. Equipment for permeability testing was described by RANALLI (1955) and ROSEN (1957). Permeability through polymeric films was also studied by FRISH (1956), HEILMAN (1956) and WAACK (1955). Evaluation of films for use as irradiation chambers has been described by BUCHBERG (1956) and WILSON (1958).

Although most of the analytical evaluation of this investigation was by infrared, some tests were made chromatographically. DIMBAT (1956) discusses the effect of column packing, temperature, detector sensitivity and other factors. An excellent discussion is included of the methods of calculation. GREENE (1957) discusses a method for NO_2 using wet molecular sieves as column packing. A reaction mechanism yielding NO provides an indirect measurement of NO_2.

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EXPERIMENTAL EQUIPMENT

The compression tests were made with a compressor–manifold–tank set-up. The manifold was constructed with stainless steel pipe, fittings, valves, etc., to permit flexibility of operation with either the compression or atmospheric sampling procedures. Teflon gaskets were fabricated for positive seals at unions and sample-tube connection points. Pipe joints were made up with Halocarbon, high-temperature stopcock grease. The sample preparation system, compression system, and 10-m photometric cell were connected by Imperial fittings from glass or pipe to $\frac{3}{8}$ in. o.d. polyethylene tubing. Tubing length was minimized wherever possible. The compressor used was a Bell and Gosset Model SYC-15-1 with carbon rings. It is a two-stage unit of 1·9 ft^3/min displacement at 1725 rev/min with maximum operating pressure 175 psig.

The atmospheric tests were made with plastic bags fabricated in the laboratory from polymeric films, except for the case of those that required special sealing and were made up by the manufacturer. These bags contained approximately 60 to 70 l. of gas and were approximately 18 × 50 in. deflated.

Analyses were made for each of the tests (compression or atmospheric) with a single pass, single beam, Perkin–Elmer Model 12B, infrared spectrometer using a sodium chloride prism and a 10-m path-length cell.

The chromatographic unit utilized a Gowmac thermal conductivity cell, Model

9285, and a Minneapolis–Honeywell recorder, Model Y153 X 18V-X-(118) with a 0 to 2 mV sensitivity.

EXPERIMENTAL PROCEDURE

Compression tests were made by preparing the desired gaseous mixture in a plastic bag and then compressing this gas mixture into a 1·1 l., 2-in. diameter, stainless steel tank to approximately 150 psig. Gas analyses were made by infrared, before and after compression, and at various time intervals thereafter.

The atmospheric test runs were made in a similar manner. Standard gas mixtures were prepared from reagent gases and tank air in the plastic bags. Initial concentrations were estimated manometrically and then an analysis was obtained by drawing the gas mixture into the evacuated 10-m cell of the infrared spectrometer. After a selected time interval, such as 20 hr, the analysis was rerun and any change in concentration of the various gaseous components was noted. In the latter stages of the evaluation some runs were made by gas chromatographic procedures. These were made to test low concentration, low volume samples.

Since the object of these tests was to determine the suitability of the plastic films as gas storage containers, non-permeability and non-reactivity were desired properties. The gases selected for study were nitrogen dioxide, sulfur dioxide, and typical hydrocarbons. Certain standard gas mixtures were selected for evaluation. These included: (a) acetone, benzene, nitrogen dioxide; (b) nitrogen dioxide, sulfur dioxide, 2-pentene; and (c) nitrogen dioxide, sulfur dioxide, 2-methyl pentane, butyraldehyde. Initial concentration of gaseous components usually ranged from 60 to 80 p.p.m. It was necessary to make these tests at these high concentrations because of the limitations of the infrared technique. Limits of concentration were established by the path-length and absorption coefficient of the material, and instrument characteristics. The gases were obtained from reagent tanks and were discharged via a short glass and polyethylene manifold directly into plastic make-up bags. Concentrations were estimated by manometric measurement and confirmed by infrared. The studies were made at room temperature which usually averaged between 70 and 75°F.

Gas–liquid chromatographic analysis was made in the following manner: a standard gas mixture was prepared in a polymeric film bag. The pollutants were added in a manner similar to that described above. The test gas-mixture in the bag was passed through a trapping column at liquid nitrogen temperature. The trapping column was operated with a packing (such as dimethylsulfolane) or in some instances without packing. The contents of the trapping column were then eluted through the packed column. Ice temperature was held for tests with hydrocarbons. The packed columns were of such material as dimethylsulfolane, dibutyl phthalate, molecular sieve, etc. The elution times of the various gas components were indicated on a recorder actuated by the detector. The time of elution and the area under the elution curve indicated a quantitative measurement of gaseous component under consideration.

COMPRESSION SAMPLING

Compression sampling was considered as a means for transferring large volumes of gas from the field to the laboratory in reasonably sized containers. The very process of compression of large volumes of gas was suspect. The purpose of the compres-

sion sampling evaluation made in this study was to determine if various gaseous pollutants were amenable to compression storage. Representative ketones, aldehydes, aromatics, saturated and unsaturated hydrocarbons were tested as well as the mineral oxides: nitrogen dioxide and sulfur dioxide.

The techniques used in this study are described above. Analyses before and after compression (150 psig) and with varying storage periods were obtained. Acetone and butyraldehyde were affected while 2-methyl pentane, benzene, and 2-pentene showed no significant change (Table 1). Nitrogen dioxide and sulfur dioxide showed appreciable losses after compression. Losses of SO_2 and NO_2 were just as high after 5 min storage as after 20 hr.

It was suspected that the compressor could be causing the loss of certain gases. To check this, mixtures of nitrogen dioxide, sulfur dioxide, 2-methyl pentene were prepared in plastic bags, analyzed, then discharged via the compressor to the 10-m cell of the infrared spectrometer to note apparent changes in concentration (Table 2).

Sulfur dioxide loss was great. The hydrocarbon was unaffected. The compressor itself was deemed a source of loss. Compression sampling was concluded to be satisfactory for hydrocarbons but not for mineral oxides. Compression testing was terminated and the emphasis was placed upon atmospheric sampling and storage of gaseous pollutants in bags of polymeric films.

TABLE 1. COMPRESSION-STORAGE

Gaseous component	Concentration (p.p.m.)		Time
	Start	End	
Benzene	117	107	20 hr
Acetone	46	41	
Butyraldehyde	145	123	17 hr
2-Pentene	41	52	
Acetone	67	44	18 hr
Benzene	88	86	
Butyraldehyde	65	52	
Butyraldehyde	66	43	20 hr
2-Methyl pentane	58	56	
Sulfur dioxide	58	11	
Nitrogen dioxide	62	11	
Sulfur dioxide	33	0	5 min
Nitrogen dioxide	36	19	

TABLE 2. COMPRESSOR EFFECT

Gaseous component	Concentration (p.p.m.)	
	Start	End
Nitrogen dioxide	67	65
Sulfur dioxide	62	30
2-Methyl pentane	77	77
Nitrogen dioxide	90	70
Sulfur dioxide	71	18
2-Methyl pentane	48	43

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TABLE 3. PHYSICAL PROPERTIES OF POLYMERIC FILMS

Film	Chemical type	Tensile strength	Tear strength	Water vapor permeability	Oxygen permeability	Miscellaneous
Mylar	Polyester (contains no plasticizer or additive)	20,000 lb/in² per 1 mil	15 g per 1 mil	0·035 g/100 in²/hr per 2 mils	0·00029 g/100 in²/hr per 2 mils	Flex life of 20,000 cycles. Easy to seal with a heat sensitive tape
Aluminized Mylar	Polyester					The aluminum coating is very thin and wears easily
Saran wrap Type 12	Polyvinylidene chloride	13,000–20,000 lb/in² per 2 mils	10–20 g per 1 mil	0·0042 g/100 in²/hr per 2 mils		Good resistance to sunlight. Difficult to seal except by special equipment
Saran wrap drumliner	Polyvinylidene chloride					Same as above
Scotchpak 20A5	Polyester (contains no plasticizer)	7800 lb/in² per 2 mils	32 g per 2 mils	0·021 g/100 in²/hr per 2 mils	0·6 g/100 in²/hr per 2 mils	Fair resistance to sunlight. Excellent folding endurance. Easy to heat seal
Aluminized Scotchpak 20A20	Polyester	8000 lb/in² per 2 mils	30 g per 2 mils	0·00082 g/100 in²/hr per 2 mils	0·025 g/100 in²/hr per 2 mils	Fair resistance to sunlight. Easy to heat seal. Best water barrier studied

ATMOSPHERIC SAMPLING

Tests were made to determine the effect of storage of single gases and mixtures of gases in plastic bags at atmospheric pressure. The properties of various polymeric films were surveyed and various materials were selected for evaluation. Table 3 summarizes some of the physical properties of the films studied.

The gases used in the study included: ketones; aldehydes; aromatic, saturated

and unsaturated hydrocarbons; sulfur dioxide and nitrogen dioxide. Certain standard mixtures of these gases were used during the tests. The basic mixture used for time dependency studies was sulfur dioxide, nitrogen dioxide and 2-pentene. This mixture contains the principal mineral oxides and a typical unsaturate. Other standard mixtures included: 2-methyl pentane, butyraldehyde, sulfur dioxide, nitrogen dioxide; and benzene, acetone, nitrogen dioxide. Initial concentration of these gases was at approximately 70 p.p.m. level.

During preliminary tests with Mylar and aluminized Mylar, the points on the time–concentration curves for a storage period exceeding 80 hr were separate independent runs. A smooth correlation was obtained from the cumulative data which was interpreted as a verification of the reliability of the experimental technique. Nitrogen dioxide was stored overnight in the same Mylar bag on different days over $1\frac{1}{2}$ months to determine the effect of repeated use (Table 4).

There is no indication of time–wear dependency. All the data were obtained during a period of high humidity.

The effect of moisture, i.e. high humidity, is important. This is demonstrated in Fig. 1. Three sets of data are given for the storage of nitrogen dioxide in aluminized

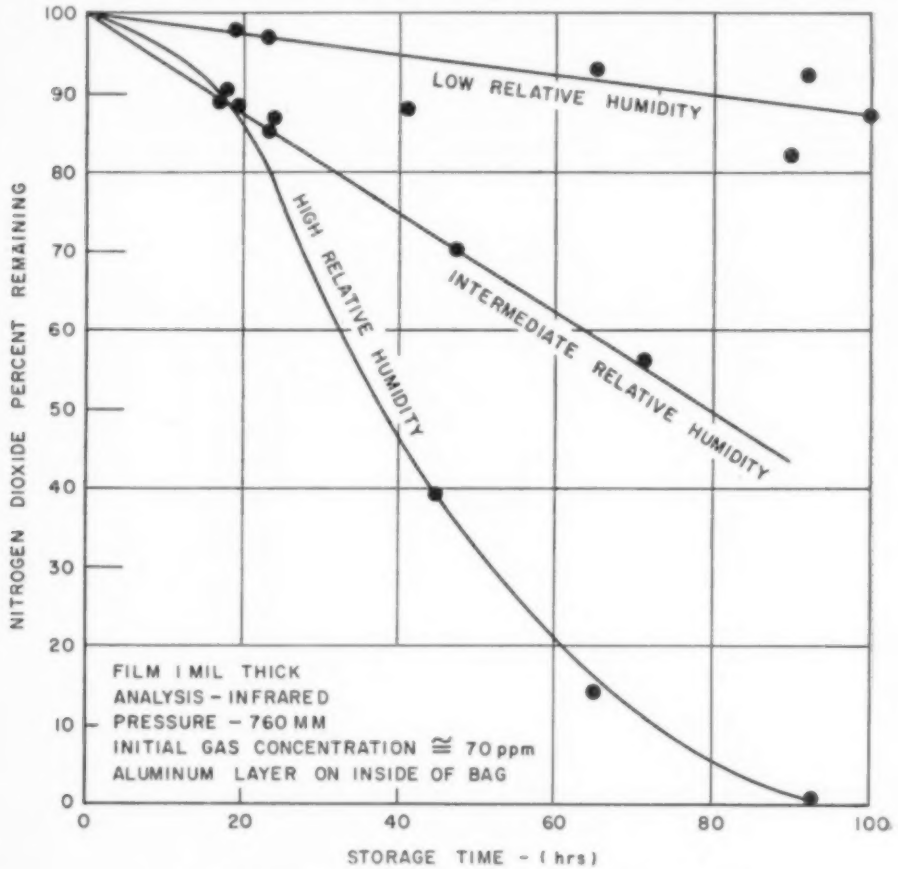

FIG. 1. Evaluation of aluminized Mylar for nitrogen dioxide storage.

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Mylar. The run made in the summer during high relative humidity periods shows a rapid decrease in measured NO_2 with time. A run showing little loss was made during the winter heating season when room air was quite dry. The intermediate values

TABLE 4

Date	Concentration (p.p.m.)		Time (hr)	% Remaining
	Initial	Final		
20 May	77	43	18	56
3 June	61	36	19	59
8 July	52	29	18	56

were obtained by artificially creating a moist atmosphere. This was accomplished by water addition to the dry tank air, which was used as diluent. The relative humidity was estimated from the infrared charts to be intermediate between that of the other two runs.

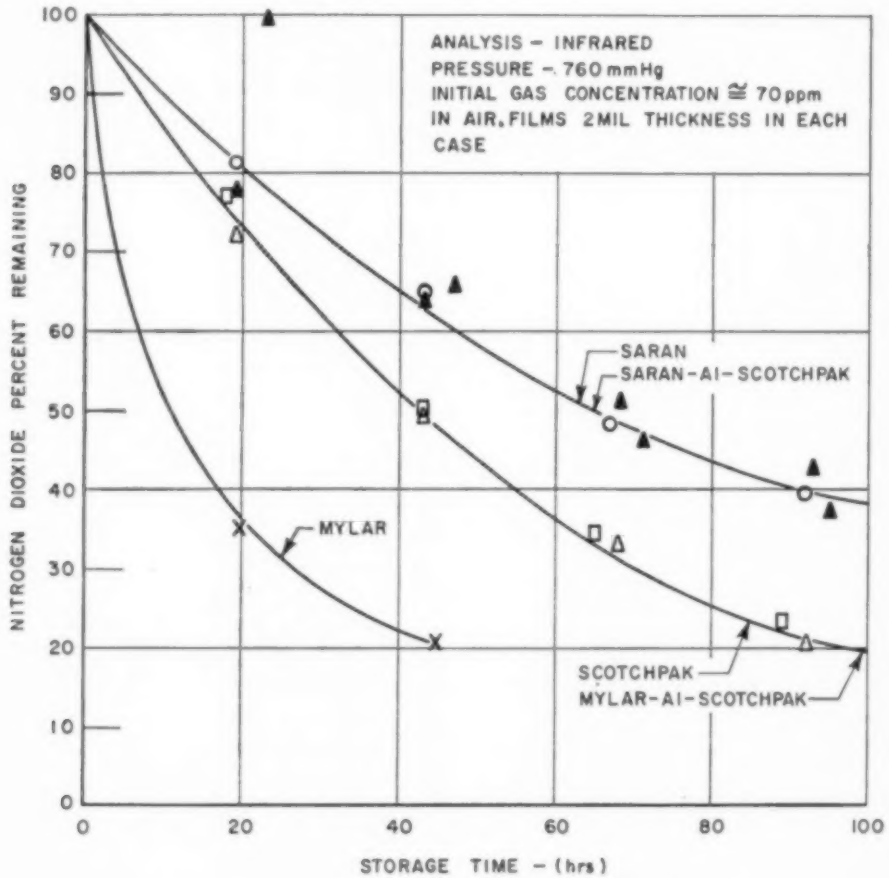

FIG. 2. Evaluation of polymeric films for nitrogen dioxide storage.

Relative humidity measurements were not made during these tests. To be meaningful they would have had to have been made in a controlled atmosphere. Daily humidity variation precluded interpretation of results. Further tests are contemplated in which the films will be studied under controlled humidity.

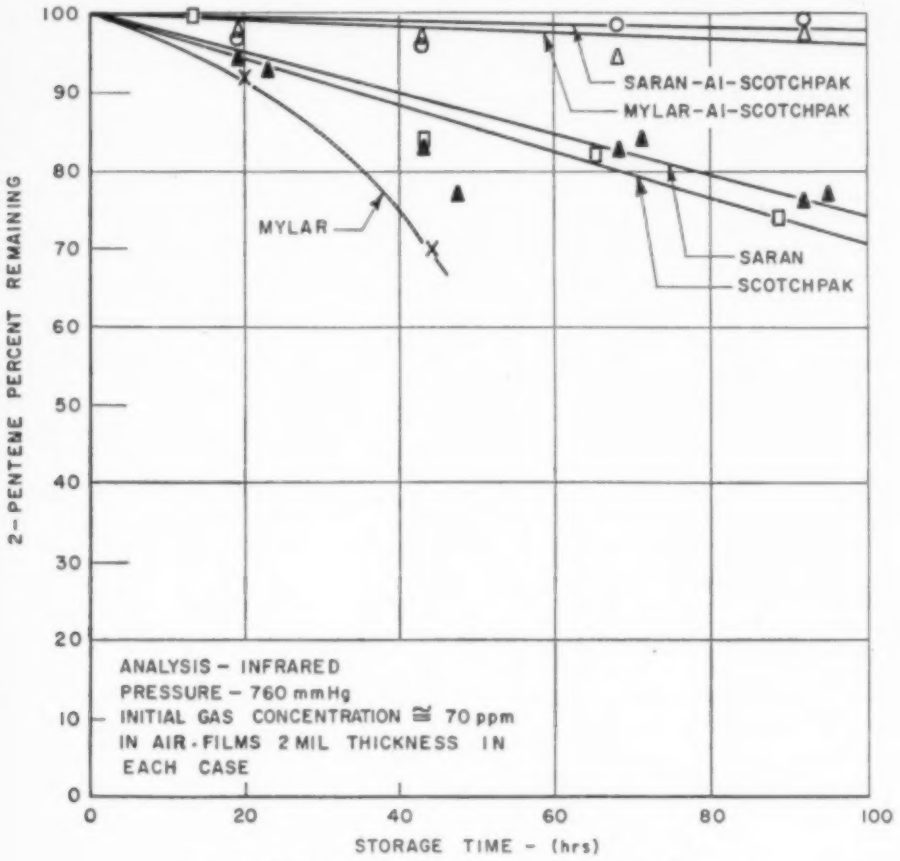

FIG. 3. Evaluation of polymeric films for 2-pentene storage.

The results of storage of nitrogen dioxide, 2-pentene and sulfur dioxide as a ternary mixture are shown in Figs. 2, 3 and 4 respectively. The presentation of time-dependency data for storage of the individual components is made to facilitate plastic film comparison. Miscellaneous tests not depicted graphically are summarized in Table 5.

In all of the studies it was found that the hydrocarbons showed only minor changes in concentration over periods of 18 to 70 hr. Acetone and benzene concentrations were slightly but consistently higher after storage, butyraldehyde and 2-methyl pentane showed little change, and 2-pentene showed minor losses. Variations may be attributed to selective diffusion of the smaller molecules. Although many tests were made, time was not available for a complete time–concentration evaluation of all the hydrocarbons in every film.

The mineral oxides, nitrogen dioxide and sulfur dioxide, were most affected.

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Decreased concentrations of these gases with time are chiefly caused by water reaction. Nitrogen dioxide drops off sharply with time (Fig. 2) in all of the films. Because of the similarity of the results for Saran and Saran–aluminized Scotchpak and Mylar–aluminized Scotchpak only three regressions are shown. Variations are within experimental accuracy.

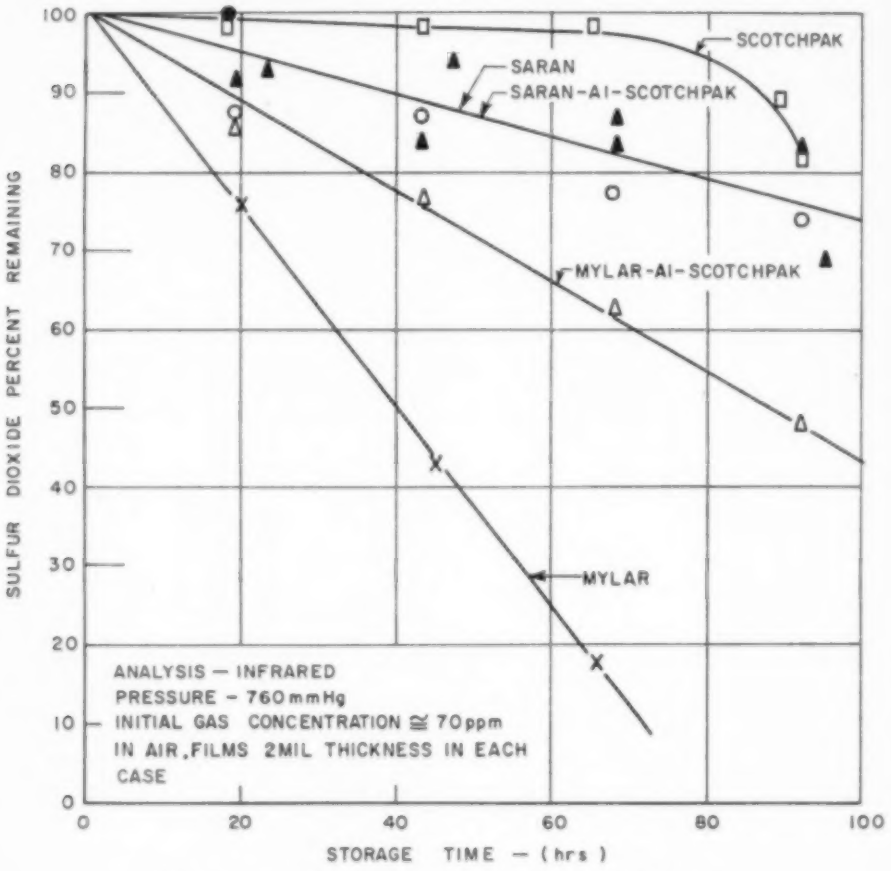

FIG. 4. Evaluation of polymeric films for sulfur dioxide storage.

The double-film bags were each made with the aluminized Scotchpak on the outside. This was found to be the best moisture barrier tested. Each film of the composite bags was 2 mils in thickness giving a total thickness of 4 mils.

Fig. 3 shows that 2-pentene was stored quite successfully. The improvement indicated for the two-film bags is attributed primarily to the double thickness. The use of aluminized Scotchpak around Mylar showed a marked improvement over the single Mylar film in storage of sulfur dioxide (Fig. 4). Similar improvement is not indicated for Saran–aluminized Scotchpak over plain Saran. Scotchpak showed good sulfur dioxide storage up to 65 hr.

Although controlled humidity conditions were not available for these tests, the comparative data presented graphically do measure relative behavior fairly well. All

TABLE 5. EVALUATION OF POLYMERIC FILMS FOR STORAGE OF GASES
Analyses: Infrared
Pressure: Atmospheric

Gaseous component	Concentration (p.p.m.) Initial	Concentration (p.p.m.) Final	Length of time (hr)	Film gauge and size
Butyraldehyde	55	50	24	Mylar (200)
	66	69	17	18 × 50 in.
Ethylene	64	63	19	
2-Methyl pentane	66	67	17	
	70	64	26	
	70	64	26	
Nitrogen dioxide	64	44	18	
Sulfur dioxide	69	68		
2-Methyl pentane	51	52		
Butyraldehyde	64	61		
Nitrogen dioxide	63	52	18	
Sulfur dioxide	58	64		
2-Methyl pentane	54	56		
Butyraldehyde	68	68		
Benzene	76	81	18	
Acetone	60	62		
Nitrogen dioxide	52	41		
Benzene	31	26	65	
Acetone	39	20		
Nitrogen dioxide	78	13		
Nitrogen dioxide	54	47	22	Aluminized Mylar (100)
Sulfur dioxide	73	78		18 × 52 in.
2-Methyl pentane	71	73		
Nitrogen dioxide	50	52	19	
Sulfur dioxide	70	77		
2-Methyl pentane	72	79		
Nitrogen dioxide	71	18	66	
Sulfur dioxide	129	24		
2-Methyl pentane	61	75		
Nitrogen dioxide	49	22	67	
Sulfur dioxide	57	30		
2-Methyl pentane	65	67	18	
Butyraldehyde	63	69		
Sulfur dioxide	78	78		
Nitrogen dioxide	46	50		
2-Methyl pentane	62	62	24	
Butyraldehyde	79	77		
Sulfur dioxide	82	41		
Nitrogen dioxide	81	38		

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TABLE 5. EVALUATION OF POLYMERIC FILMS FOR STORAGE OF GASES (*continued*)

Gaseous component	Concentration (p.p.m.)		Length of time (hr)	Film gauge and size
	Initial	Final		
Acetone	55	63	18	
Benzene	84	86		
Nitrogen dioxide	43	41		
Acetone	56	66	67	
Benzene	80	95		
Nitrogen dioxide	66	16		
Nitrogen dioxide	64	39	19	Saran (200)
Acetone	56	69		36 × 36 in.
Benzene	72	76		
Nitrogen dioxide	66	37	20	
Acetone	51	73		
Benzene	79	79		
Nitrogen dioxide	76	59	17	
Sulfur dioxide	81	75		
2-Methyl pentane	65	65		
Butyraldehyde	49	51		
Nitrogen dioxide	49	34	19	Saran drumliner (200)
Acetone	64	64		36 × 36 in.
Benzene	81	75		
Nitrogen dioxide	76	50	18	
2-Methyl pentane	70	67		
Sulfur dioxide	85	77		
Butyraldehyde	59	54		
Nitrogen dioxide	70	41	18	
Sulfur dioxide	66	65		
2-Pentene	69	65		
Nitrogen dioxide	60	30	17	Scotchpak (200)
Acetone	56	78		36 × 32 in.
Benzene	70	74		
Nitrogen dioxide	66	0	23	
Sulfur dioxide	65	44		
2-Methyl pentane	60	64		
Butyraldehyde	49	50		
Nitrogen dioxide	51	0	17	Aluminized Scotchpak
Acetone	54	57		(200)
Benzene	63	68		36 × 34 in.
Nitrogen dioxide	76	8	17	
Sulfur dioxide	83	73		
2-Methyl pentane	66	68		
Butyraldehyde	50	45		
Nitrogen dioxide	64	6	18	
Sulfur dioxide	77	55		
2-Pentene	76	80		

the results shown except for Mylar and one set for Saran were made simultaneously. Hence the humidity conditions were similar.

Moisture will be an important, unavoidable factor in field sampling. Soluble gases such as nitrogen dioxide and sulfur dioxide will tend to dissolve and the extent of solution will be a function of surface moisture–gas phase equilibrium. A dry film and gas will not show this variation of apparent mineral oxide content. Moisture, size of gas molecule and film pore dimensions influence diffusion or permeability.

If the relative humidity is low on sampling but subsequently increases, moisture buildup will occur in some plastic bags on storage. The use of a sampling bag made of two films, one impermeable to the gaseous components and a second to moisture, may be necessary for certain tests.

These studies show that gases such as sulfur dioxide and nitrogen dioxide may be stored for periods up to 24 hr by proper selection of films. Hydrocarbons may generally be stored for longer periods of time with minimum loss.

STORAGE IN STEEL AND GLASS VESSELS AT ATMOSPHERIC PRESSURE

Stainless steel and glass containers are commonly used for storage of gases. They are convenient and readily available. Steel containers are usually used for sampling of high-pressure sources. Glass containers are used at atmospheric pressure. Experience with dynamic calibration of continuous recorders of sulfur dioxide has shown that glass may be a source of error. Although the earlier compression sampling tests in stainless steel were not successful, the error was attributed to the compressor. Consequently, glass and stainless steel were evaluated as storage containers at atmospheric pressure by the techniques being employed in this study.

Table 6 is a summary of the results of storage of the standard gaseous mixture (NO_2, SO_2, 2-pentene in dry tank air) in glass. Two 22-l. round-bottom flasks were used. Large diameter glass tubing of equal length to each flask was used as a manifold to minimize flow losses and ensure equalization of gaseous components. Aluminum foil was placed around the rubber stoppers used to seal the flasks to eliminate gas to rubber contact. After the initial mixtures were prepared and analyzed, the tanks were recharged to atmospheric pressure with dry, tank air. This decreased the partial pressure of the pollutants in the flask and necessitated correction of the concentration measured by the infrared. Losses in glass were quite significant.

A similar test was made with a standard 34-l. stainless steel tank using the same gas mixture. Table 7 shows that all of the gaseous components including the oxides of nitrogen and sulfur were retained. The slight increase in measured concentrations over calculated concentrations may be considered within experimental error. The results are another indication that in the compression tests the losses were caused by the compressor. It would appear that where gases of the kind studied here are obtained in evacuated stainless steel tanks from sources at higher pressure, such as in gas transmission lines, the samples are reliable after storage for periods up to approximately 40 hr. This is not the case for glass vessels.

MOISTURE PERMEABILITY OF POLYMERIC FILMS

Moisture buildup is a problem in gaseous storage and analysis. Use of laminates or double-film sampling bags was suggested and it was deemed advisable to establish the relative merit of the films under study as moisture barriers.

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The different films have varying permeability to water vapor. To provide a comparison it was necessary to test all the films simultaneously under similar conditions of atmospheric humidity. The storage period had to permit a sufficient interval for moisture penetration at atmospheric humidity, but short of saturation conditions.

Each of the plastic bags being studied was filled with approximately 60 l. of dry tank air. The infrared spectrum was scanned at the start of the run and after 17 hr.

TABLE 6. EVALUATION OF GLASS FOR STORAGE OF GASES
Glass containers: two 22-l. round-bottom flasks in parallel
Analyses: infrared
Pressure: atmospheric

Gaseous component	Storage time				
	Initial (p.p.m.)	24 hr		41 hr	
		(p.p.m.)	(% Remaining)	(p.p.m.)	(% Remaining)
	Based on air dilution and initial analyses				
Nitrogen dioxide	45	38		32	
Sulfur dioxide	39	33		28	
2-Pentene	35	30		26	
	Actual analyses				
Nitrogen dioxide	45	21		14	
Sulfur dioxide	39	22		20	
2-Pentene	35	29		23	
	Based on corrected volume				
Nitrogen dioxide			55		44
Sulfur dioxide			67		71
2-Pentene			97		90

The portion of the water band of the spectrum from 5·6 to 6·2 μ is depicted in Fig. 5. The blank shows the initial absorption caused by the water vapor in the atmosphere surrounding the external optics of the infrared spectrophotometer. To enhance clarity of presentation only portions of each of the individual curves are given at 6·15 μ. This shows that the best moisture barrier was aluminized Scotchpak. Mylar had the least resistance, although aluminized Mylar (100 gauge) ranked next to aluminized Scotchpak in effectiveness (Table 8). Obviously the aluminum serves to seal the polymeric film pores. Fortuitously after 17 hr none of the bags reached saturation.

It was decided that two-film bags or polylaminates would be prepared and evaluated using the aluminized Scotchpak in conjunction with other films.

DARK REACTION

A dark reaction may take place when gases such as 2-pentene, nitrogen dioxide and sulfur dioxide are stored. Aerosols or condensation products are possible as products

of the reaction mechanism. This possibility was checked by use of the Sinclair–Phoenix, forward-scattering aerosol, dust, and smoke photometer, Model JM-1000.

TABLE 7. EVALUATION OF STAINLESS STEEL FOR STORAGE OF GASES
Stainless steel tank, 34-l. capacity
Analyses: infrared
Pressure: atmospheric

Gaseous component	Storage time			
	Initial (p.p.m.)	24 hr		41 hr	
		(p.p.m.)	(% Remaining)	(p.p.m.)	(% Remaining)
	Based on air dilution and initial analyses			
Nitrogen dioxide	74	60		49	
Sulfur dioxide	65	53		44	
2-Pentene	71	57		47	
	Actual analyses			
Nitrogen dioxide	74	63		54	
Sulfur dioxide	65	60		50	
2-Pentene	71	63		51	
	Based on corrected volume			
Nitrogen dioxide			100		100
Sulfur dioxide			100		100
2-Pentene			100		100

TABLE 8. MOISTURE PERMEABILITY

Film	Gauge	Experimental rank	Manufacturer's data water permeability 10^{-4}g/100 in^2 per hr
Aluminized Scotchpak	200	1	8·2
Aluminized Mylar	100	2	—
Saran, plain	200	3	42
Saran, drumliner	200	4	—
Scotchpak	200	5	210
Mylar	200	6	710

Two preliminary tests were made in which gaseous pollutants mentioned above were mixed with air and stored in Hastings' aluminized Mylar bags. In the first test, about 60 p.p.m. of each gas was added to the bag. After 17 hr a ten-fold increase in scattering was found. In the second test, the Sinclair–Phoenix reading indicated a decrease. Because of the inconclusive nature of these two tests additional runs were made at a later stage of the study with bags less permeable to moisture. At this point gas storage in composite polymeric films was under examination. Therefore the standard gas

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mixture was stored in each of two multi-film plastic bags. In the first bag, sample 1. the inner layer was Saran Wrap 12, 200 gauge, surrounded by aluminized Scotchpak, 200 gauge. In the second bag, sample 2, the inner layer was Mylar, 200 gauge, and the outer layer aluminized Scotchpak, 200 gauge. A mixture of gas containing 70

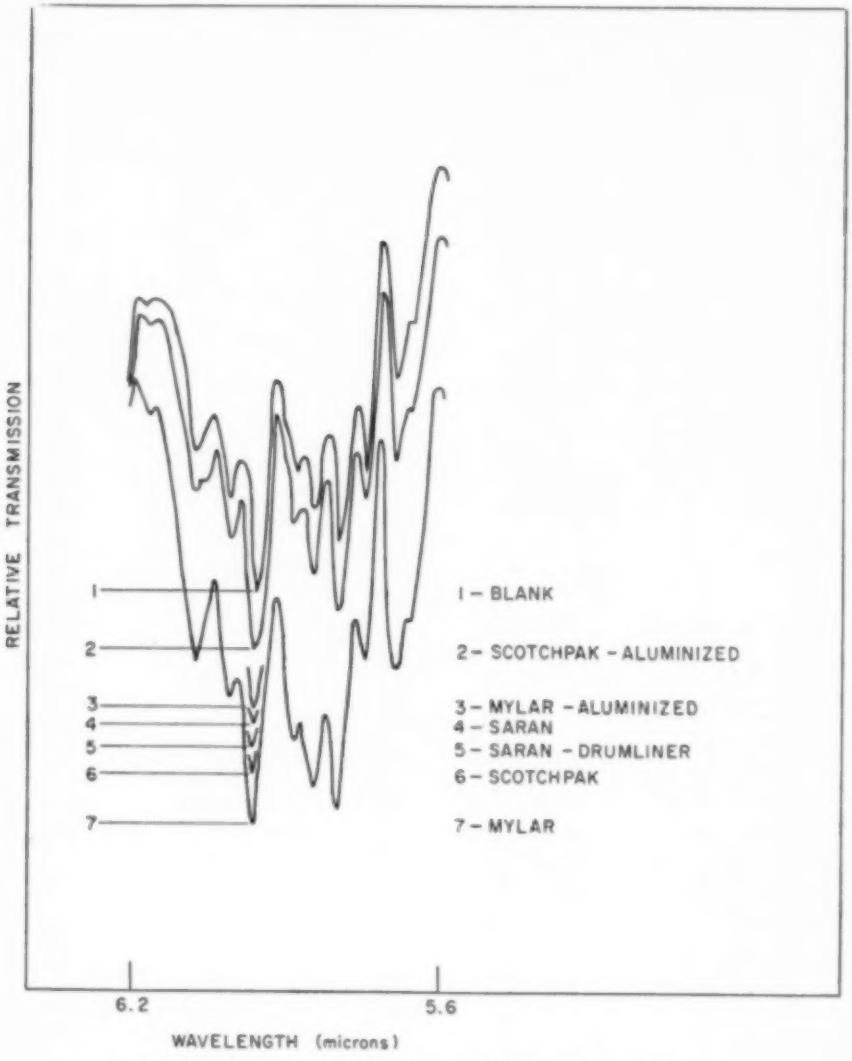

FIG. 5. Moisture permeability polymeric film (17 hr storage).

p.p.m. each of nitrogen dioxide, sulfur dioxide, and 2-pentene was added to each of the bags. Initial readings were taken and these were followed by readings at 24 and 46 hr intervals (Table 9).

Aerosol formation was not demonstrated and it was concluded that dark reaction was not occurring under the experimental conditions.

TABLE 9. DARK REACTION EVALUATION
Sinclair–Phoenix photometer readings

Sample	0 hr	24 hr	46 hr
Room air	0·8	1·3	1·25
Sample 1	0·4	0·0	—
Sample 2	0·0	0·0	0·0

GAS–LIQUID CHROMATOGRAPHIC ANALYSIS CONCLUDING REMARKS

It has already been stated that the levels of gas concentration required for the evaluation of the various materials was approximately 70 p.p.m. The level of concentration was necessitated by analytical considerations. It was desirable to make tests at lower concentrations approximating atmospheric conditions. Gas–liquid chromatography offers a means of working at lower gas concentrations but analytical procedures are not developed to a point permitting broad, quantitative measurement.

Methods of GLC have been developed for low boiling hydrocarbons. Therefore tests were made using a small, 15-l. capacity Scotchpak bag and a diluted sample of Phillips mixture No. 40. The latter is a multicomponent mixture of saturated and unsaturated hydrocarbons. In initial tests, a 20-ft dimethylsulfolane column was used at ice temperature. For purposes of this discussion only one gas component will be used as reference: *n*-butane. Dry tank air was used to dilute a mixture No. 40 sample to give 0·1 p.p.m. *n*-butane. A well-defined, good-sized peak was obtained and it appeared that the component could be measured at approximately 4 p.p.h.m. After 18 hr of storage the concentration of hydrocarbon was essentially the same. Use of plastic film containers and chromatographic analysis for low concentrations of hydrocarbons up to C_5 appears feasible. The C_6 and higher hydrocarbons will require development of the analytical scheme.

Although various attempts have been made to measure sulfur dioxide and nitrogen dioxide by gas–liquid chromatography no reliable method is available. Some trials were made at the close of this study to obtain SO_2–NO_2 calibration. Triethylene glycol seemed to pass sulfur dioxide but calibration could not be made because of inconsistent results. Dibutyl phthalate and molecular seives, 5A, were also tried as SO_2–NO_2 trapping materials without much success. It should be noted that these were very abbreviated trials without extensive evaluation of all the parameters. It is believed, however, that this analytical method in conjunction with polymeric film storage bags is a promising combination. Polarographic procedures may also hold promise for some specific gaseous components.

CONCLUDING REMARKS

Compression sampling was found to be a satisfactory method for hydrocarbons but to result in high losses of sulfur dioxide and nitrogen dioxide. Moisture was found to be a major factor in the loss of gases stored in bags of polymeric film. This was especially true for nitrogen dioxide and sulfur dioxide. Hydrocarbons were not similarly affected. Use of two-film plastic bags may be advantageous for certain air sampling problems. One film could be impermeable to the gas of primary interest and the second to moisture.

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Small volume plastic bags and gas–liquid chromatography appear to offer a useful combination for field sampling of air pollutants.

The occurrence of a dark reaction could not be demonstrated after 46 hr storage of a sulfur dioxide, nitrogen dioxide and 2-pentene mixture under experimental conditions. Storage of this same ternary mixture in glass and steel at atmospheric pressure showed high loss of the mineral oxides in glass but no significant loss in steel.

Additional study of gas storage in plastic films under conditions of controlled humidity is necessary. These studies are contemplated.

Acknowledgements—The following manufacturers provided samples and technical information about the polymeric films used in this study: E. I. du Pont de Nemours and Company, Wilmington, Delaware—Mylar; Hastings and Company, Philadelphia, Pennsylvania—aluminized Mylar; Dow Chemical Company, Midland, Michigan—Saran Wrap 12 and Saran drumliner; Minnesota Mining and Manufacturing, Minneapolis, Minnesota—Scotchpak 20-A-20 and aluminized Scotchpak 20-A-5.

The study was supported by contract SAph 69635 with the Department of Health, Education and Welfare, Taft Sanitary Engineering Center, Cincinnati, Ohio.

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SPECTROSCOPIC ANALYSIS OF INDUSTRIAL EMISSIONS FOR NITRIC OXIDE, NITROGEN DIOXIDE AND SULFUR DIOXIDE*

A. J. HAAGEN-SMIT†, VINCENT D. TAYLOR‡ and MARGARET F. BRUNELLE**

(*Received* 8 *May* 1959)

Abstract—Together with smoke density meters, the automatic recording NO and SO_2 meters are valuable tools in the prevention of excessive emissions of air pollutants in flue gases. The NO, SO_2 recorder makes available a research tool for the study of formation and control of oxides of nitrogen and sulfur. The close relation between flame temperature and NO formation should open the way for interesting studies in plant operation.

The removal of excess water, dust and sulfuric acid from the flue gas by condensation and electrostatic precipitation is of general application, and has led to a more disturbance-free operation of many different types of automatic instruments such as sulfur dioxide, nitric oxide, carbon monoxide, carbon dioxide and oxygen analyzers.

THE emission of oxides of nitrogen is recognized as a factor in the formation of Los Angeles type smog. As part of a research program sponsored by the Southern California Edison Company a study was made of processes leading to a decrease in the emission of oxides of nitrogen in stack effluents (BARNHART and DIEHL, 1959; HAAGEN-SMIT and CHADWICK, 1959).

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Chemical measurements are unsatisfactory because of fluctuations in stack gas composition, and unless a large number of single determinations are made, the experimental error may be great. In addition, the chemical methods are time consuming. Especially in the study of the effect of furnace conditions on the formation of oxides of nitrogen the need for a monitoring device was strongly felt. After changes have been made in the combustion conditions, it is difficult to decide when a steady state, favorable to spot analysis, has been attained. In the laboratory investigations a large number of catalytic agents were tested, and here also a quick and accurate analysis was needed to record the nitric oxide and sulfur dioxide content of inlet and outlet gases.

Several difficulties had to be overcome before a continuous registration was possible. Combustion gases contain substantial quantities of water, sulfur dioxide and dust, and to make matters worse, enough sulfuric acid to raise the dew-point to 300° F. The removal of water, dust and sulfuric acid was accomplished by condensation, followed by electrostatic precipitation. A millipore filter following this train was included as a safety factor to protect the infrared analyzer in case of failure of the precipitator. No visible dust had collected on this filter after several months of use.

This arrangement has been used before a Consolidated Electrodynamics Corpora-

* Paper presented at the Air Pollution Symposium of the American Chemical Society, 134th National Meeting, Chicago, Ill., 7–12 September, 1958.

† California Institute of Technology, Pasadena, Calif.

‡ Massachusetts Institute of Technology, Cambridge, Mass.

** Los Angeles County Air Pollution Control District, Los Angeles, Calif.

tion ultraviolet spectrophotometer, indicating the NO_2 content of the flue gas. We found that the NO_2 concentration is less than 20 p.p.m. (v/v), and that most of the oxides of nitrogen are in the form of NO. In order to measure the NO, it was necessary to oxidize the NO to NO_2 with ozone. By scanning with different quantities of ozone, a continuous registration of NO_2 by the ultraviolet spectrophotometer could be obtained. Although satisfactory measurements were made, it appeared more simple to measure NO directly by infrared spectroscopy. We found the Liston–Becker Model 21 infrared analyzer quite suitable for this task, and two of these instruments have been in constant operation for over 1 year without interruption.

DESCRIPTION OF APPARATUS

The arrangement of the infrared analyzers and the purification train is shown in Fig. 1. The condensation coil, fabricated from stainless steel tubing of ¼ in. dia-

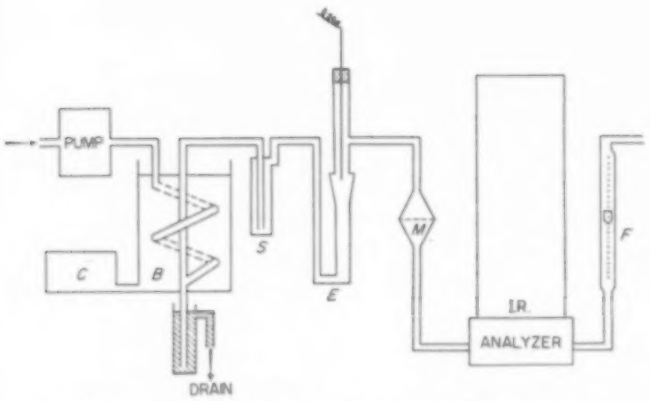

FIG. 1. Sampling system for infrared analysis of flue gas.
Flue gas stream is passed through a condenser held at 4° C, then through an electrostatic pecipitator to remove excess water and dust before passage through the infrared analyzer.

C—refrigeration unit
B—constant temperature water bath
S—safety trap
E—electrostatic precipitator
M—millipore filter
F—flow meter

meter, is submerged in a constant temperature water bath held at approximately 4° C. This can be accomplished with ice. However, since our goal was a fully automatic analyzer with a minimum of servicing required, we found it expedient to use a small, hermetically sealed refrigeration unit manufactured by Tecumseh Products Company, Tecumseh, Michigan, Model P6112L. The condensed water is removed through a gas-tight overflow device.

The flue gas passes next through a precipitator made of Pyrex glass (Fig. 2). The glass tube consists of two parts, connected by a 29/42 standard taper platinum clad joint, which is grounded. The electrode is a carbon steel rod of 3/32–1/8 in. diameter. Power is supplied by a unit manufactured by Raytheon Manufacturing Company, Waltham, Massachusetts, which delivers an output of 10,000 V d.c., at very low amperage.

The purified gas is then passed through a millipore filter, AA white, plain, 0·47 mm, backed by a No. 1 Whatman filter paper. These are held in position with a wax seal (U.S.P. beeswax and paraffin 1 : 1) between two glass funnels. Another satisfactory glass filter holder has been described (MADER *et al.*, 1950), in which ground glass surfaces between which the filter is placed are held together by a special clamp. Filter holders are available from the Millipore Filter Corporation, Watertown 72, Mass., but these are usually fabricated of metal, and do not afford the visibility or corrosion resistance of glass construction. The gas then enters the analyzer. On the exit side of the analyzer a rotameter indicates the flow rate, which is kept at approximately 2 l/min.

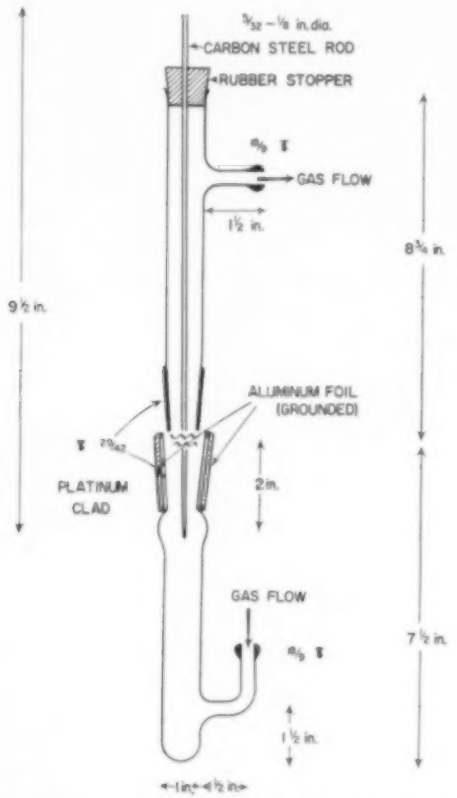

FIG 2. Precipitator for removal of dust from flue gas stream.

The apparatus has been operated on suction by placing a pump at the far side of the train. However, it is preferable to have a positive pressure in the system, obtained by placing a pump between the source and the apparatus. We now use a pump obtained from A. O. Beckman, Inc., Fullerton, Calif., Model Z 300. It is a heavy duty diaphragm pump, with positive displacement, powered by a ¼ h.p. motor, using 115 V, 50–60 A. All surfaces are of stainless steel or synthetic rubber to prevent corrosion. The bearings are permanently lubricated.

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STANDARDIZATION

Nitric oxide

Standard gas mixtures obtained from the Matheson Company, Inc., East Rutherford, N.J., are used to calibrate the instrument. The zero, or background, gas is composed of 1000 p.p.m. SO_2, 10·5 per cent CO_2 and the balance N_2. Using this mixture, the instrument is set at zero by means of a built-in, manual standardization device. When gas is to be used as fuel it may be preferable to omit the SO_2 from the standard gas mixture. The up-scale gas is a mixture of 500 p.p.m. NO, 10·5 per cent CO_2 and the balance nitrogen.

Sulfur dioxide

For SO_2 calibration the procedure is reversed, using the standard NO mixture for the zero and the standard SO_2 mixture for up-scale.

EFFECT OF CO_2 ON NO CONCENTRATION DETERMINED BY THE INFRARED ANALYZER

Carbon dioxide is included in the standard gas mixtures in a concentration of 10·5 per cent because the flue gas has been observed to vary in CO_2 concentration between 8 and 13 per cent. To determine the effect of CO_2 concentration on the infrared readings for NO, varying amounts of CO_2 were introduced into the sample stream, and any change in the infrared reading was recorded. The CO_2 was introduced through a flow meter, and its concentration could be adjusted by varying the flow rate while maintaining a constant flow rate of 1675 ml/min through the infrared analyzer. The data are shown in Table 1.

TABLE 1. CO_2 CONCENTRATION VS. INFRARED READINGS NO ANALYZER

CO_2 added (ml/min)	% of total as CO_2	Infrared reading (p.p.m. NO)	ΔNO (p.p.m.)
0	10·0	545	—
19	11·1	550	5
80	14·8	580	35
184	21·0	600	55
290	27·3	625	80
453	37·0	640	95
0	10·0	520	—
92	15·6	560	40
208	22·3	590	70

Background: flue gas, containing approximately 10 per cent CO_2.
Fuel: ½ oil, ½ gas.
Boiler: No. 2.

The infrared reading obtained with flue gas alone was used as a base, and any variation from this reading was recorded as Δ NO in parts per million. Since the base level varied, each run was computed from its own base level. The total concentration of carbon dioxide in the flue gas was calculated, using the assumption of

10 per cent CO_2 present in the original flue gas. The fuel during these experiments consisted of one-half oil and one-half gas.

From these experiments we may conclude that any deviation in the infrared reading of NO concentration due to normal fluctuation of the CO_2 is not significant, since in the concentration range usually encountered in power plant operation the deviation is less than 5 per cent.

EFFECT OF CO ON SO_2 AND NO INFRARED ANALYZERS

During the normal efficient operation of a power station carbon monoxide is virtually absent from the stack gases. However, under certain conditions which favor inefficient combustion, such as the transition from oil to gas or a reduction in the excess oxygen, carbon monoxide may be formed.

To test response to carbon monoxide, known quantities of CO were introduced into the gas stream entering the analyzers. The results are shown in Fig. 3. The response was found to be the same whether flue gas or standard gas mixtures were used as the background.

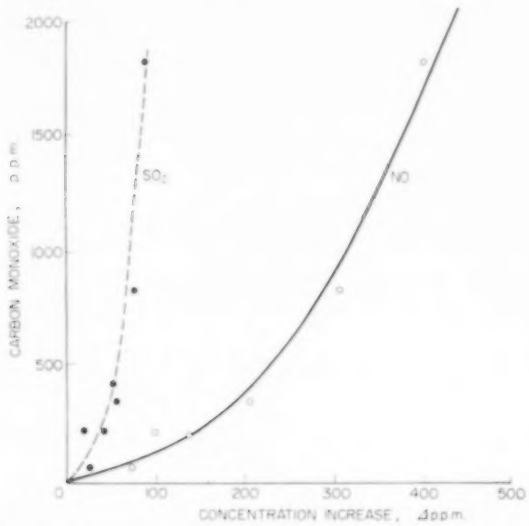

FIG. 3. Response of infrared analyzers to carbon monoxide.
Background gas composed of 10·5 per cent carbon dioxide in nitrogen. The indicated increase in spectrophotometer reading upon introduction of known amounts of CO to the background gas is designated as "Δ p.p.m.". Response of both SO_2 and NO analyzers is shown.

Both SO_2 and NO analyzers are sensitive to CO and will register CO as SO_2 or NO, respectively. While this interference is objectionable if one wants to measure only NO or SO_2, the CO can be eliminated by passing the gas stream over a combustion zone at approximately 1500° F. However, carbon monoxide is a sensitive indicator of combustion conditions, and by passing the gas stream through our purification train we have successfully operated a Mine Safety Appliances Infrared Analyzer for carbon monoxide in addition to our regular analyzers.

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EFFECT OF SO_2 ON NO CONCENTRATION DETERMINED BY THE INFRARED ANALYZER

Flue gas from the combustion of oil and gas contains varying concentrations of SO_2, and the effect of these variations on the NO readings was determined by adding different quantities of SO_2 to the flue gas containing 500 p.p.m. SO_2. The resulting data are shown in Table 2.

It is shown that in the concentration range of 0–2750 p.p.m. SO_2, the NO readings are not affected significantly.

TABLE 2. EFFECT OF SULFUR DIOXIDE ON INFRARED READINGS OF NITRIC OXIDE IN FLUE GAS

SO_2 added (ml/min)	Total SO_2 (p.p.m.)	Infrared reading (p.p.m. NO)
0	500	500
2	1500	510
4·5	2750	515

No. 2 Unit; Fuel: ½ oil, ½ gas.
Background: flue gas containing approximately 500 p.p.m. SO_2.

ANALYSIS OF STACK GASES BY INFRARED SPECTROSCOPY

To illustrate the use of the instrument, a few examples have been selected of data obtained during boiler operation (Figs. 4, 5 and 6). The sensitive response of the instrument to furnace operating conditions is indicated in Fig. 4, by the appearance

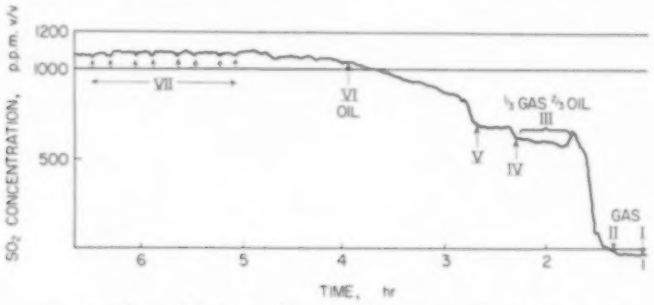

FIG. 4. Effect of fuel on sulfur dioxide concentration in flue gas.
Reading from right to left, the Roman numerals indicate stages in the transition from 100% gas (I and II) to 100% oil (VI and VII). Changes in SO_2 concentration (p.p.m.) as indicated by the infrared spectrometer are clearly shown. Arrows indicate dips in SO_2 concentration caused by the normal soot-blowing cycle, and illustrate the sensitivity of the infrared response.

of small dips (arrows) which are caused by dilution of the stack gas with air blown into the stack for the removal of soot. In this figure the increase in SO_2 concentration during a change from gas to oil is shown.

Figs. 5 and 6 illustrate results obtained while testing the effect of operational variables on nitric oxide formation. In both cases the effect on NO formation was easily recorded by the infrared spectrometer. Fig. 6 includes data from chemical analyses made during the test, using the modified Griess method (SALTZMAN, 1954) and the phenoldisulfonic acid method (BEATTY *et al.*, 1943; GOLDMAN and JACOBS,

1953). In general, all three methods agree. However, more variation between individual analyses is shown by the chemical methods than by the continuous infrared measurement. Subsequent tests of each of the methods on a standard gas mixture

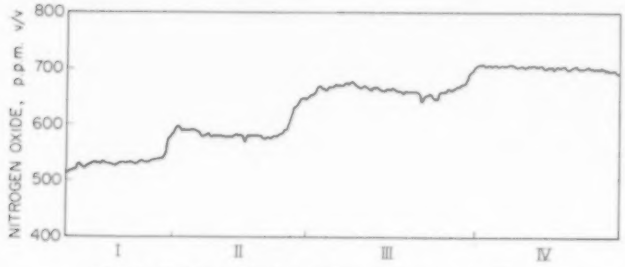

FIG. 5. Nitric oxide formation vs. burner position.
The NO concentration in the stack gas at four different burner positions is shown, and illustrates the effectiveness of relatively simple adjustments in the reduction of NO, as well as the ease with which the results of such changes are indicated by the infrared analyzer.

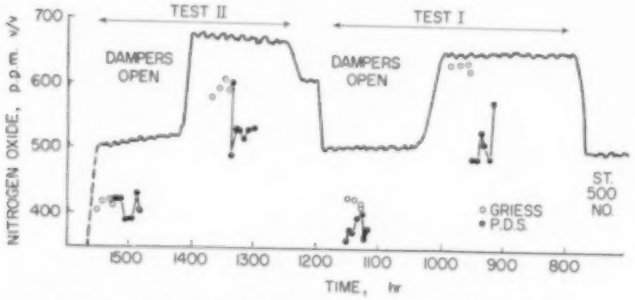

FIG. 6. Infrared vs. chemical analysis of nitric oxide in flue gas.
Results of chemical analysis by modified Griess and phenoldisulfonic acid methods are plotted on a chart from the infrared spectrometer made during two tests on the boiler. Reading from right to left, a trace of standard gas containing 500 p.p.m. NO is followed by Tests I and II. Note the general correlation between the three methods and fluctuations in chemical analyses while the infrared spectrometer indicated a steady concentration in NO.

showed deviations of approximately 10 per cent for the chemical methods, while the infrared varied by less than 2 per cent. The deviations observed in the chemical methods are probably due to inconsistencies in the sampling methods, and temporary disturbance of the furnace air. The continuous record of the infrared points out these fluctuations, and provides a more representative picture of the happenings in the furnace. In addition, the infrared spectrometer is more sensitive to variation in the NO concentration than either of the chemical methods.

Acknowledgements—The authors would like to express their appreciation to Beckman Instruments, Inc., to Consolidated Electrodynamics Corporation, and to A. O. Beckman, Inc., for their co-operation in making their instruments available for experimental research; to Mr. R. H. DUNDAS of Bechtel Corporation for his part in designing and building the portable analyzer unit, and to Mr. JOE HARA of Truesdail Laboratories for his valuable assistance.

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THE LONGEVITY OF THE PHYTOTOXICANT PRODUCED FROM GASEOUS OZONE–OLEFIN REACTIONS*

WILFRED NIELS ARNOLD†
(*Received* 24 *April* 1959)

Abstract—Gaseous mixtures of an olefin and ozone were blown at constant rate through a 32 ft tube of uniform cross section. A small aquatic plant was placed at prescribed intervals within the tube. The phytotoxicants produced from the ozonization of both 3-heptene and 2-pentene were shown to be unstable. The distribution of plant damage within the exposure tube indicated the longevity of the phytotoxicant.

The reduction in chlorophyll content of fumigated plants was used as a quantitative measure of damage. The results suggest that the decay of the phytotoxicant follows a first order or pseudo-first order reaction. The half-life of the phytotoxicant from ozonated 3-heptene is ¼ hr while the phytotoxicant from ozonated 2-pentene has a much shorter half-life. This difference in stability can be explained in terms of the " zwitterion " mechanism.

INTRODUCTION

A UNIQUE type of air pollution damage to vegetation of the Los Angeles area was reported by MIDDLETON *et al.* in 1950. Leafy vegetables are extremely sensitive to this type of injury; the glazing symptoms have been associated with the oxidizing nature of the Los Angeles atmosphere. HAAGEN-SMIT *et al.* found that plant damage symptoms, resembling those occurring in the field, could be produced on test plants by the reaction products of certain olefins with ozone. The phytotoxicant escapes positive identification at this date. The present investigation has been concerned with the unstable nature of the phytotoxicant and in particular with the rate at which the material decomposes. The rate of decay of the phytotoxicant should give some insight into the composition and structure of the molecule.

SCOTT *et al.* studied the gas phase reactions of ozone with a number of olefins by infrared spectroscopy. They found that the " zwitterion " mechanism advanced by CRIEGEE for the liquid phase chemistry was successful in explaining the reaction products, although ozonides were minor products in the gas phase. Under this mechanism the attack at the double bond by ozone is followed by a splitting of the addition product to yield aldehydes and zwitterions. Several subsequent reactions by the zwitterions are possible. The stable end products include aldehydes, alcohols, organic acids, oxides of carbon, and ozonides.

Recent studies by DARLEY and co-workers revealed that the stable ozonides of 1-pentene and 2-pentene are not phytotoxic at concentrations of 3 to 5 parts per million (p.p.m.) while the phytotoxicant from the ozone–olefin reaction is unstable at concentrations of less than 1 p.p.m.

In the present investigation a large excess of olefin was reacted with ozone so that the addition reaction of ozone to the double bond was virtually completed within a

* Thesis presented to the Graduate Division, University of California, Los Angeles, in partial fulfillment of the requirements for the degree of Master of Science.

† Formerly Junior Specialist, University of California, Riverside. Present address: Department of Botany, Cornell University, Ithaca, New York.

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matter of seconds. It was desirable to achieve an ozone-free system because plants are damaged by ozone alone. Plants were fumigated at intervals in a dynamic system and the distribution of damage was used as an indication of relative concentrations of the toxicant.

MATERIALS AND METHODS

The unique fumigation apparatus was 32 ft long and was constructed with 4 ft sections of 3 in. outer diameter glass tubing, sealed with plastic tape and located in a building supplied with activated carbon filtered air. A perforated aluminum plate was placed at each joint to decrease air layering. The behavior of an ammonium chloride cloud blown down the tube indicated that the flow pattern was reasonably free from turbulence. Under constant flow rate and uniform rate of introduction of reactants, the concentration of any compound at a particular site should remain constant in such an apparatus.

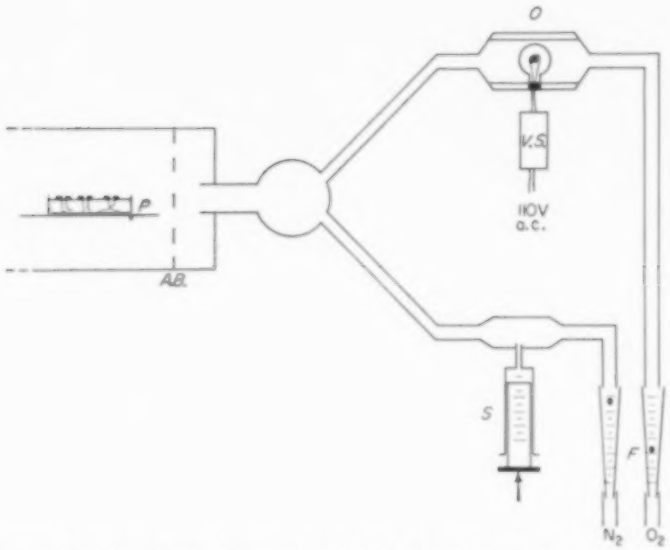

FIG. 1. Apparatus for introducing the reactants into the fumigation tube. *AB* Aluminum baffle; *F* Flow meters; *O* Ozonizer; *P* Petri dish; *S* Syringe; *VS* Voltage stabilizer.

The flow system for the introduction of the gaseous reactants is shown in Fig. 1. Gas flows were measured by flow meters that were recalibrated by displacing air through the meters with a measured volume of water. The ozonizer consisted of a small ultraviolet lamp surrounded by a glass jacket through which passed tank oxygen, dried with anhydrous calcium chloride. Variations in the output of the ozonizer were minimized by placing a voltage stabilizer in the circuit. The ozone concentration was calculated from the iodine released from neutral 0·1M phosphate-buffered 20 per cent potassium iodide.

The olefin was dispensed from a hypodermic syringe by a plunger that was driven by a brass rod, geared to a small electric clock. The syringe was surrounded by a water

jacket which was maintained at 5°C. A stream of nitrogen vaporized the olefin from the tip of the syringe. The olefins used in these experiments were technical grade 3-heptene and 2-pentene.

It has been mentioned that the phytotoxicant produced from the ozone–olefin reaction has not been positively identified. Much of the difficulty which has been encountered in analysis is undoubtedly due to the unstable nature of the phytotoxicant, which is demonstrated in the present investigation. Bioassay is the only sure method available for quantitative work with the phytotoxicant. ERICKSON and WEDDING showed that a small aquatic plant *Lemna minor* L. was injured by ozonated hexene. They found a good correlation between the reduction in chlorophyll content and the duration of exposure. The size and sensitivity of the plant made it ideal for this investigation.

Plants were floated in open, $2\frac{3}{4}$ in. petri dishes which were supported by thin aluminum plates. These plates were 8 in. long and their width was a little less than the inside diameter of the tube so that the level of the plants in the petri dish was in line with the horizontal diameter of the tube. Plants were exposed at prescribed intervals along the tube. Replicates were obtained at each exposure point by dividing each petri dish with a small aluminum strip held in place by paraffin wax. The wax was covered by the bathing solution of the plants. Dishes were aligned in the tube so that the strips ran lengthwise. The assembled tube was covered with sheets of black paper. The plants were exposed under these conditions for periods of about 24 hr. Control plants were placed in the dark, near the tube. The same set of control plants was used for all positions in the tube.

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The reduction in chlorophyll content of fumigated plants was used as a quantitative measure of plant damage. All of the plants in any one sample were ground in a Potter homogenizer with 1 ml of acetone. After adding another 5 ml of acetone the slurry was mixed and then centrifuged. The clear supernatant was decanted into a 10 ml stoppered, volumetric flask and the volume was made up with acetone. The optical density of this solution was measured at 665 mμ. Damage was expressed as a percentage by the ratio: reduction in optical density over optical density of control extract. By carefully selecting uniform, three-fronded plants in groups of fifteen it was possible to obtain extracts with optical densities that varied by as little as 1 per cent and rarely by more than 5 per cent. The variation between duplicates of fumigated plants was generally slightly higher.

The absorption spectrum of an acetone extract from *Lemna minor* has peaks at 432 mμ and 665 mμ. Absorbance measurements were made at the higher wave length because the absorption at 665 mμ is primarily due to chlorophyll-*a*. At 432 mμ there is interference from other leaf pigments; however, a close agreement was obtained between damage determinations at the two wave lengths.

Plants were grown in nutrient solutions contained in 10 l. glazed porcelain crocks. The greenhouse was supplied with carbon filtered air. Temperatures ranged between 20°C and 30°C and the light intensity at midday was typically 3000 ft candles. The nutrient solution, which was changed daily, was made with tap water to which was added potassium nitrate, magnesium sulphate, potassium monobasic phosphate, and chelated iron, in amounts comparable to half-strength Hoagland's solution. Growth was most vigorous at a pH between 6 and 7; the pH was adjusted to within this range with 7 per cent nitric acid.

RESULTS

Experiments with 3-heptene

Preliminary trials with 3-heptene and ozone revealed that there was no significant decrease in damage from one end of the tube to the other unless the residence time was

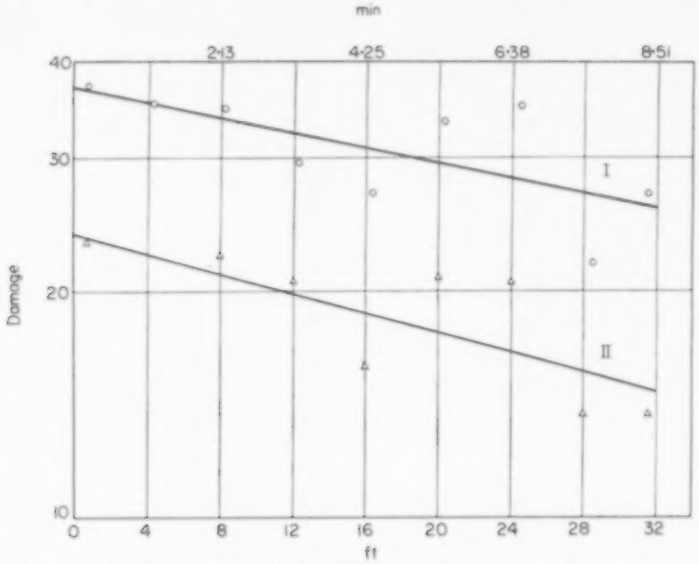

FIG. 2. The decay of the phytotoxicant from 3-heptene and ozone; residence time 8·51 min. The damage scale is logarithmic, expressed as percentage reduction in chlorophyll content compared with unfumigated controls.

at least 8 min. Trials I and II were conducted with a flow rate of 4·95 l./min ; the residence time was 8·51 min. Trials III and IV were carried out at a flow rate of

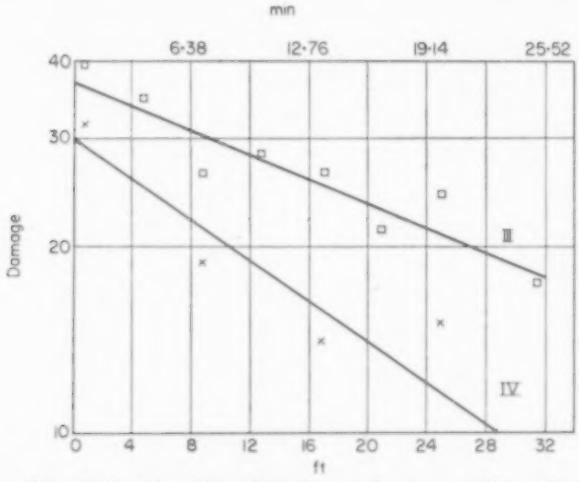

FIG. 3. The decay of the phytotoxicant from 3-heptene and ozone; residence time 25·52 min. The damage scale is logarithmic, expressed as percentage reduction in chlorophyll content compared with unfumigated controls.

1·65 l./min to provide a residence time of 25·52 min. The lower air flow was obtained by bleeding to waste all but one-third of the individual ozone–oxygen and olefin–nitrogen streams before mixing.

If there had been no reaction the final concentrations would have been 2·3 p.p.m. of ozone and 35·0 p.p.m. of 3-heptene. The cracking of rubber under tension is a highly sensitive and specific test for the presence of ozone. Small strips of rubber were placed at intervals within the tube. After 1 hr at the higher flow rate there was slight cracking on the test piece 1 ft from the point of introduction of the reactants. There was no cracking at 4 ft so the initial ozone–olefin addition reaction had run almost to completion within the first 2 or 3 ft of the tube.

The results of four fumigations with 3-heptene and ozone are presented in Figs. 2 and 3. Each point represents the mean damage of two samples at that position. Positions are expressed as distances from the point of introduction of the reactants and as the length of time that the reaction has been allowed to proceed. Calculations based on a least-squares covariance analysis of the data are presented in Table 1.

TABLE 1. FUMIGATIONS WITH OZONE (2·3 p.p.m.) AND 3-HEPTENE (35 p.p.m.)—EQUATIONS TO THE STRAIGHT LINES OF BEST FIT

Trial	Equation	Correlation coefficient
I	$\log D = 1{\cdot}5694 - 0{\cdot}004866\,S$	$r = 0{\cdot}6778^{**}$
II	$\log D = 1{\cdot}3748 - 0{\cdot}006499\,S$	$r = 0{\cdot}7125^{*}$
III	$\log D = 1{\cdot}5690 - 0{\cdot}009974\,S$	$r = 0{\cdot}9374^{**}$
IV	$\log C = 1{\cdot}8467 - 0{\cdot}004593\,S$	$r = 0{\cdot}9280^{**}$

D = damage
C = chlorophyll content
S = distance in feet

* Significant at 0·05 level
** Significant at 0·01 level

Because Trial IV contained a sample (at 31·6 ft) with no damage the results were analyzed according to chlorophyll content instead of damage, as in previous trials. The straight line (IV) in Fig. 3 is a close approximation obtained indirectly from the equation to chlorophyll content.

In the course of an experiment the room temperature was recorded every 45 min. The mean temperature and standard deviation for each trial are: I, 18°C (6·7°); II, 13·8°C (9·8°); III, 23·7°C (4·5°); IV, 25·7°C (5·5°).

Experiments with 2-pentene

A trial was conducted with 2-pentene and ozone with a residence time of 8·51 min. The concentration of 2-pentene was 45·0 p.p.m.; the ozone concentration was 2·3 p.p.m. The mean damage at 1 ft was 20 per cent. The level of damage fell rapidly with distance along the tube so that most of the samples were undamaged.

Another fumigation was carried out at a residence time of 2·5 min. The concentrations were: 1 p.p.m. ozone and 100 p.p.m. 2-pentene. The results of this trial are presented in Fig. 4. The equation to the straight line of best fit is: $\log D = 1{\cdot}7404 - 0{\cdot}003925\,S$ and the coefficient of correlation, $r = 0{\cdot}8814$ (significant at 0·001 level).

Experiments with natural pollution

It was observed that plants exposed to naturally polluted Riverside air were damaged. The symptoms, separation of fronds, discoloration and dehydration of tissue, were

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similar to the symptoms of ozonated olefin injury (Fig. 5). On one occasion plants that were exposed to outside air for 2 days contained 20 per cent less chlorophyll than plants that remained in the filtered greenhouse.

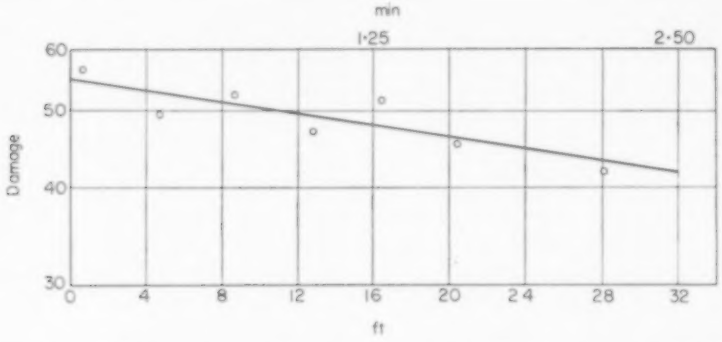

FIG. 4. The decay of the phytotoxicant from 2-pentene and ozone; residence time 2·5 min. The damage scale is logarithmic, expressed as percentage reduction in chlorophyll content compared with unfumigated controls.

DISCUSSION

One of the simpler sequences that the complex ozone–olefin reaction could undergo is a series of consecutive reactions. The steps could be represented as follows:

$$\text{Ozone} + \text{olefin} \xrightarrow{k_1} A \xrightarrow{k_2} B \xrightarrow{k_3} C \longrightarrow$$

The constants k_1, k_2, k_3, represent the specific reaction rate constants and A, B, C are the successive intermediates. k_1 for 3-heptene is 0·13 p.p.m.$^{-1}$min^{-1}, and for 2-pentene is 0·24 p.p.m.$^{-1}$min^{-1} (STEPHENS, 1958). By using a concentration of the olefin in large excess of the ozone concentration the time required for almost complete reaction of the ozone can be reduced to a matter of seconds. The analysis can be further simplified when but one of the consecutive reactions is limiting. If, for instance, the reaction $A \longrightarrow B$ were 100 times faster than the reaction $B \longrightarrow C$ then the rate determining step for the disappearance of A and the formation of C would be $B \longrightarrow C$ and the system could be analyzed as a pseudo-first order reaction.

If the phytotoxicant decays in this manner and if damage is proportional to concentration then the rate of decrease in damage $-\frac{dD}{dt}$ would be given by:

$$-\frac{dD}{dt} = kD$$

where D is the amount of damage, t = time, and k is the velocity constant. This equation, upon integration, yields:

$$\ln D = -kt + C$$

Thus, by plotting log damage against time, a straight line would be obtained.

The data of these trials have been treated in this manner. Significant correlations between the logarithm of damage and reaction time were obtained although the pattern shows some oscillation towards the far end of the tube. From the evidence at

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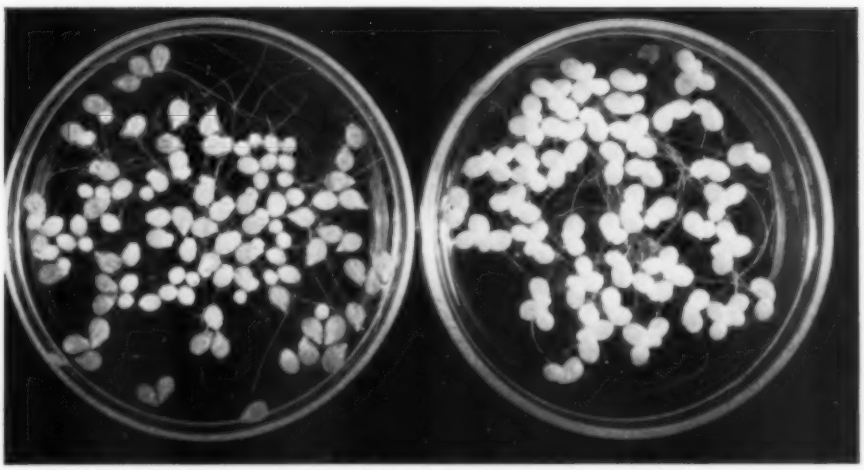

FIG. 5. Damage to *Lemna minor* L. from the reaction products of 3-heptene and ozone: left, control; right, treated.

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hand the decay of the phytotoxicant appears to follow either a first order or a pseudo-first order reaction. The period of half-life ($t_{1/2}$) can be calculated from the statistical equation in terms of distance. This figure can be converted into units of time by dividing by the velocity of the gases in the particular trial. Values for half-life are given in Table 2. The rate constant k was determined from the relationship:

$$t_{1/2}=\frac{0{\cdot}693}{k}$$

TABLE 2. FUMIGATIONS WITH OZONE (2·3 p.p.m.) AND 3-HEPTENE (35 p.p.m.)—RATE CONSTANT AND HALF-LIFE

Trial	Exposure period (hr)	Half-life of phytotoxicant (min)	k for 1st order decay of phytotoxicant (min^{-1})
I	24	16·5	0·042
II	19	12·3	0·056
III	25	24·1	0·029
IV	24	11·0	0·054
Averages		16·0	0·045

The trial (Fig. 4) with the phytotoxicant from 2-pentene gives a half-life of 6 min. This figure is open to considerable error due to extrapolation. But, from the two experiments with 2-pentene and ozone it is evident that the life of phytotoxicant from 2-pentene is much shorter than that from 3-heptene. This would account for the lack of damage from ozonated 2-pentene that HAAGEN-SMIT *et al.* observed under their conditions and for the positive results that DARLEY *et al.* obtained only when the residence time was short.

The evidence presented in this paper is consistent with " zwitterion " mechanism suggested by SCOTT and co-workers. The splitting of the addition product from 3-heptene and ozone would yield radicals C_3 and C_4, whereas the 2-pentene addition product would yield C_2 and C_3 radicals. The radicals of longer chain length would probably be more stable and thus the phytotoxicant from 3-heptene would conceivably be longer lived than that from 2-pentene.

SUMMARY

The phytotoxicants from ozonated 3-heptene and ozonated 2-pentene were shown to be unstable. The half-life of the phytotoxicant from 3-heptene is ¼ hr while the half-life of the 2-pentene phytotoxicant is much shorter.

The unstable nature of the phytotoxicant is but one part of the dynamic situation that exists in the polluted atmosphere of the Los Angeles Basin. Insight into the numerous chain reactions can be developed systematically by studying such isolated steps, in the laboratory, under steady state conditions.

Acknowledgements—The financial support of the Smoke and Fumes Committee of the American Petroleum Institute is gratefully acknowledged. The advice and encouragement of Drs. JOHN T.

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MIDDLETON and ELLIS F. DARLEY, under whose guidance these studies were carried out, are deeply appreciated. The Franklin Institute group granted permission to quote unpublished data on rate constants; appreciation is extended to Dr. EDGAR R. STEPHENS for helpful discussion.

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THE SPATIAL DISTRIBUTION OF AIR POLLUTION IN SHEFFIELD, 1957–1959

J. PEMBERTON*, MARJORIE CLIFTON, J. K. DONOGHUE†, D. KERRIDGE and WINIFRED MOULDS
The Medical Research Council Group for Epidemiological Research on Respiratory Disease (Air Pollution), University of Sheffield
(*Received* 20 *May* 1959)

Abstract—(1) A study of the distribution of smoke and sulphur dioxide in Sheffield over a 2-year period has been made with a maximum number of 30 daily sampling instruments in the second year.

(2) Pollution levels were related inversely to elevation but the most important factor, particularly for smoke, was found to be the population density in the area round the instrument. Industria sources accounted for much of the sulphur dioxide.

(3) Maps have been drawn upon which the pollution means for one complete year, and also for one summer and two winter periods, have been entered at the site of each instrument. The yearly means or smoke for 1958–59, April to March, ranged from 6 to 51 mg/100 m³, and for sulphur dioxide from 2·1 to 15·2 parts per 100 million. Pollution during the second winter was considerably heavier in most areas than in the first.

(4) Although at most sites there was an increase in pollution during the second year as compared with the first, there was evidence of a decrease in smoke in an area near the city centre recently designated as Smoke Control Area No. 1. However, sulphur dioxide levels here as elsewhere showed an increase during the second year.

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THE above M.R.C. Group was established to study air pollution in relation to respiratory disease. This paper presents the findings about the spatial distribution only of air pollution in Sheffield. Temporal changes, and the relationship between air pollution and health, will be dealt with in subsequent papers. Experiments in connexion with the siting of instruments and the reliability of results are reported in another paper in this issue (CLIFTON *et al.*, 1959).

The most detailed study of air pollution in a British city so far reported was that carried out over a period of 3 years in Leicester (H.M.S.O, 1945) using twelve volumetric instruments. A report on the London fog of December, 1952, was published by the Ministry of Health (H.M.S.O., 1954) giving results from twelve volumetric instruments for 9 days. A survey of air pollution by the London County Council from 1954 to 1956 based on seven volumetric instruments was included in the Medical Officer of Health's report for 1957 and later published (GORE and SHADDICK, 1958). The monthly Atmospheric Pollution Bulletin issued by the Department of Scientific and Industrial Research (D.S.I.R.) gives mean monthly air pollution concentrations in many parts of the British Isles. In the Sheffield study, by using the same technique throughout and having a comparatively large number of instruments, air pollution could be related to the health of the population in different parts of the city and the results of day-to-day changes noted.

* Now Professor of Social and Preventive Medicine, Queen's University, Belfast.
† Now at U.K. Atomic Energy Authority, Springfields Works, Salwick.

THE TOPOGRAPHY OF SHEFFIELD AND THE DISTRIBUTION OF POPULATION

The topography of Sheffield is more complicated than the shallow basin-like configuration of Leicester and London, as there are variations in altitude from 100 to

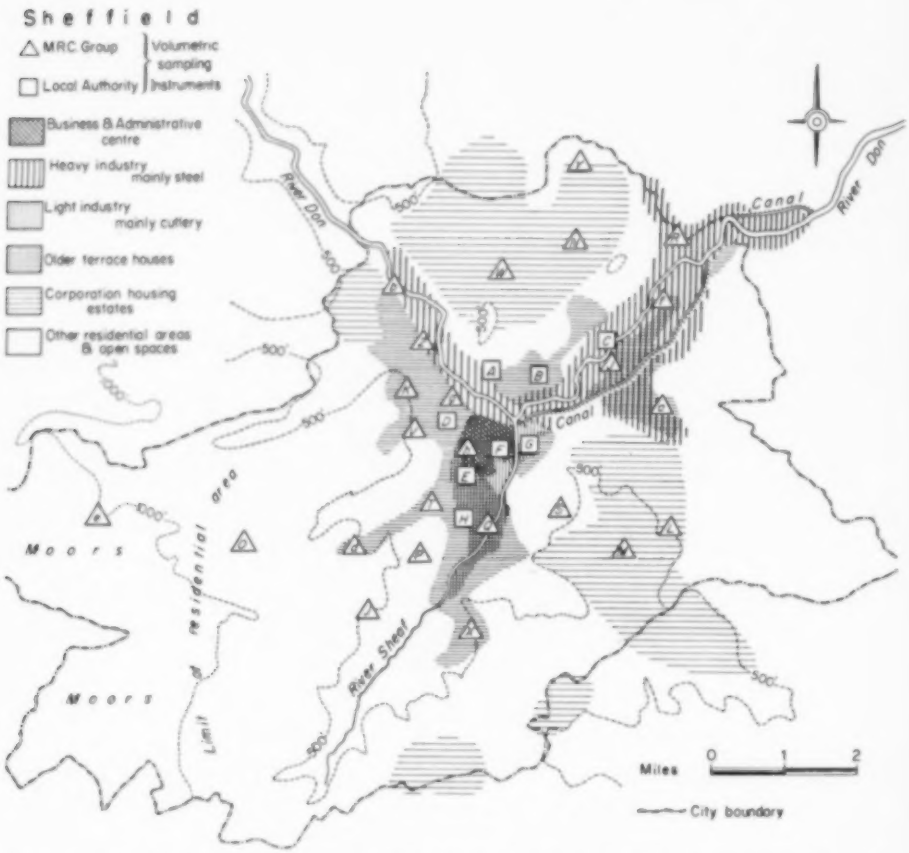

FIG. 1. Map of Sheffield with contours at 500 ft (152 m) and 1000 ft (305 m) elevation. Triangles show the sites of pollution sampling instruments operated by the M.R.C. Research Group, and squares indicate those operated by the local authority.

over 1400 ft (30 to 427 m). The main river valley system resembles the letter " Y ". The upper two limbs are formed by the Don and the lower limb by its tributary the Sheaf (see Fig. 1). The city, originating at the junction of the two rivers, has grown during the past 150 years along these three valleys. Factories are concentrated along the valleys because of the closeness to water and the availability of canals, roads and railways. In consequence some of the oldest and most densely populated residential districts are found in these low-lying areas (see Fig. 2). The heaviest industrial concentration is along the north-east limb of the " Y ", in the lower Don valley. Here most of the steel works are to be found. The better residential areas have been built

on rising ground to the south-west away from the industrial valleys, where the prevailing wind comes from the agricultural and moorland areas of north Derbyshire.

North of the Don lies a plateau rising to 500 ft (152 m) where large housing estates were built between 1918 and 1939, with further extensions since 1945. Similar large housing estates have been built on high ground rising to over 700 ft (213 m) on the south-east and south.

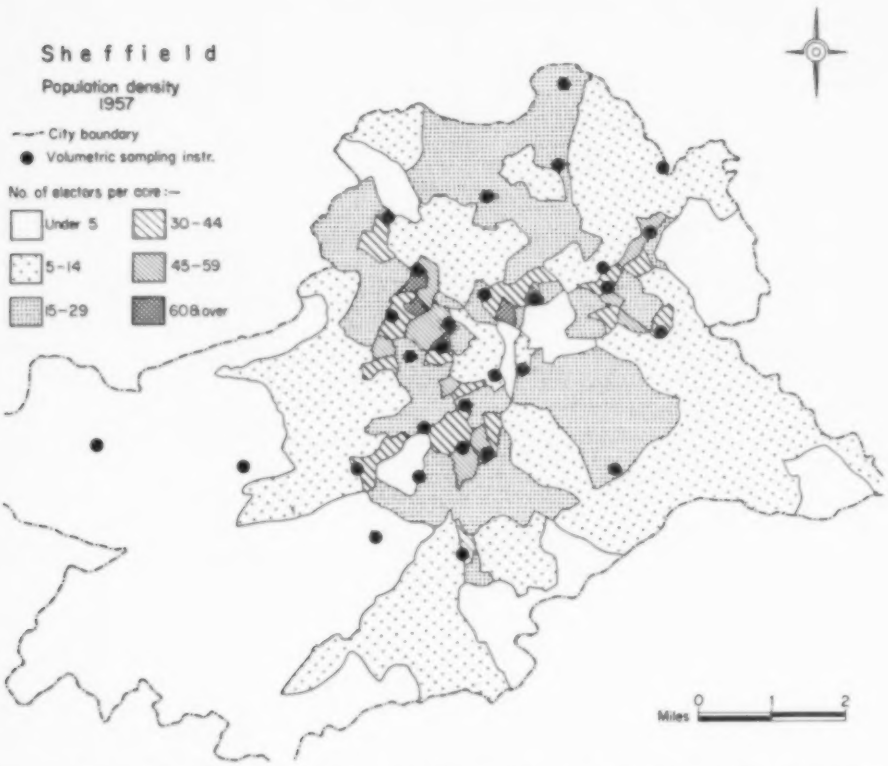

FIG. 2. Map of Sheffield showing relative population densities in 1957. The number of electors per acre in each polling district was calculated, and adjacent polling districts with similar densities were combined.

Fig. 1 shows the geographical features of the city, the distribution of industry and the various types of residential district. It also shows the sites of the instruments measuring air pollution, each with a code letter by which the site can be identified in the table.

The area enclosed by the city boundary is 39,586 acres (16,020 hectares), but this includes many square miles of open moorland in the west. For this reason the figure of 12·9 persons per acre at the 1951 census is somewhat misleading. The total population in 1951 was 512,850. Population densities in the electoral wards vary from 2·4 (in the ward which includes the above-mentioned moorland) to 62·3 near the centre. In Fig. 2 the distribution of population in 1957 is shown, using the number of electors as total population figures were not available.

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The importance of topography in relation to pollution has been stressed by GARNETT (1957) though her measurements were made with a different type of instrument.

METHODS USED TO MEASURE POLLUTION

The apparatus used to measure air pollution was that developed by the Fuel Research Station of the D.S.I.R. (1957), run for 24 hr periods, except at week-ends when few Sunday visits were possible. This apparatus measures the amount of smoke and of acid gases, mainly sulphur dioxide, in the air (to within plus or minus 14 per cent for smoke and 10 per cent for sulphur dioxide) (see CLIFTON *et al.* (1959) in this issue). A metered volume of air, approximately 60 ft³ (1·7 m³) in the 24 hr, is drawn through an inlet consisting of an inverted funnel 2 in. (5·1 cm) in diameter. Particles of a diameter greater than about 20μ fall past the funnel and are unlikely to enter the apparatus. All particles capable of entering the alveoli of the lungs (i.e. those up to about 8μ) can enter the apparatus and also some particles up to 20μ which can certainly reach the upper respiratory passages and possibly the bronchi. Larger particles, normally trapped in the nose, are unlikely to be of importance in bronchial or pulmonary disease, and the apparatus is therefore suitable for studying air pollution in relation to these diseases.

The air is drawn first through a filter paper (Whatman No. 1) which removes most of the particulate matter, and then through a Dreschel bottle. Here it is bubbled through 40 ml of a solution of 1-vol hydrogen peroxide the pH of which has been adjusted to 4·5, whence it passes through a standard gas meter.

The methods used to determine the amounts of pollution from the filter paper and hydrogen peroxide solution were as follows:

(a) The stain made by the smoke on the filter paper was converted to a weight of deposit in a given volume of air by measuring photoelectrically the amount of reflectance from the stain, compared with that of a clean filter paper on the same background. A suitable reflectometer is manufactured by Evans Electroselenium Ltd., Westminster Bank Chambers, Bishop's Stortford, Herts. Using this reflectance figure and the volume of air from which the smoke was obtained in a formula given by the D.S.I.R. (1958), the result could be expressed in mg of smoke/100 m³ of air sampled.

(b) The sulphur dioxide in the air reacts with the hydrogen peroxide in the Dreschel bottle to produce sulphuric acid. Other acids and alkalis are also trapped by the solution. These are generally present in very much smaller concentrations than sulphur dioxide and therefore the " total titratable acid " is usually expressed in terms of sulphur dioxide.

The hydrogen peroxide solution containing this acid was titrated with N/250 sodium hydroxide solution using " B.D.H. 4·5 " indicator (manufactured by British Drug Houses Ltd.). The amount of sodium hydroxide solution required to neutralize the acid, and the volume of air sampled, were used in a formula to obtain the number of parts of sulphur dioxide per 100 million parts of air.

NUMBER AND DISTRIBUTION OF INSTRUMENTS

At the beginning of this survey the Sheffield City Health Department was already operating eight of these daily volumetric instruments, mainly in the heavily polluted central area. The Health Committee agreed to purchase a further twenty-seven instruments which were placed at the disposal of the M.R.C. Group. The first three of these were installed in December 1956 and during the next 18 months 19 more instruments were placed in different parts of Sheffield, the remainder being used for experimental work and replacements. This gave a total for the city of thirty daily readings, since the Health Department made their results available to the Group.

In siting the instruments the guiding principles were to place them in populated areas to obtain representative samples of air breathed by the people living in the city, and to avoid placing the instruments close to large sources of pollution. One instrument was placed high on the moors on the west to indicate minimum levels for the area. Since the electoral wards were the areas on which many of the figures for mortality and morbidity were based, they were taken into account in selecting sites

but the number of instruments was not sufficient to cover all the larger, less populous wards and pollution estimates were made for these where possible.

The period of 24 hr for collection of samples is now in general use as the shortest practicable, when the apparatus has to be visited to change the filter paper and solution. Instruments are available which change automatically but these are expensive and need much more maintenance than the simple and reliable standard D.S.I.R. apparatus.

The ideal aimed at was to change filter papers and solution daily, including Sundays, but this was possible at only four sites. At three others arrangements were made to switch off the pump on Sunday so that a true reading for the previous 24 hr was obtained, but the remaining instruments were left running over the week-end and the pollution in each of the 24 hr periods was assumed to be the same as the average for the 48 hr. This problem will be discussed in a separate communication.

The Group was given permission to install instruments in schools, hospitals, local authority clinics, a factory, and several private houses, and at seven of the sites volunteer helpers attended to the instrument at week-ends.

AVERAGE LEVELS OF POLLUTION IN SHEFFIELD OVER DIFFERENT PERIODS

In Table 1 results are given for all the instruments in regular use in Sheffield by the M.R.C. Research Group and the local authority. The reference code used on the map (Fig. 1) is given for each site, with its elevation, an indication of the type of area in which it is situated, and an index of population density. The latter was derived from the official list of polling districts giving the number of electors in each for 1957. The area of each polling district was estimated from a map by means of a planimeter, and the number of electors per acre calculated. From these figures the map in Fig. 2 was prepared, and the index of population density for each site in Table 1 is the assessed average number of electors per acre in an area of $\frac{1}{2}$ mile (0·8 km) radius round the site.

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Although the first instruments set up by the M.R.C. Group (in addition to the eight already operated by the local authority) were started in December 1956 it was not until the beginning of April 1957 that another eight were running, making sixteen in the city. These were in almost continuous operation for the next 2 years. During the second year (April 1958 to March 1959 inclusive) thirty instruments were in operation including the original sixteen.

In calculating yearly means, when any month's readings were incomplete the following formula was used to provide an estimate of the missing figure and avoid bias:

$$\frac{\text{(that month's mean for all instruments)} \times \text{(mean of all known months for the instrument concerned)}}{\text{(year's mean for all instruments)}}$$

In addition to the yearly means, Table 1 contains means for summer and winter periods. In the Leicester Report, periods of 5 months were taken to represent summer and winter. When the Sheffield results were examined it was clear that June, July and August were much alike in having very low pollution and the addition of May and September would have blurred the picture. Similarly in November, December and January the pollution was at its heaviest. In order to obtain the best contrast it was decided to take only 3 months to represent each season: June, July and August for summer, and November, December and January for winter.

TABLE 1. LIST OF SITES OF DAILY POLLUTION SAMPLING INSTRUMENTS IN SHEFFIELD WITH REFERENCE CODES, TYPE OF AREA, ELEVATION, POPULATION DENSITY AND MEANS OF SMOKE AND SULPHUR DIOXIDE MEASUREMENTS OVER DIFFERENT PERIODS

Site of instrument	Map code	Elevation (ft)	Type of area*	Index of population density†	Pollution (Smoke = mg/100 m³; SO_2 = p.p. 100 million)												
					Means for										Mean of 2 winters		D.S.I.R. Bulletin identification No.
					1 year, April–March				Winter		Summer		Winter				
					1957–58		1958–59		1957–58		1958		1958–59				
					Smoke	SO_2	Smoke	SO_2	Smoke	SO_2	Smoke	SO_2	Smoke	SO_2	Smoke	SO_2	
Northern																	
Beck Road	*Y*	300	R	20	—	—	34	8·0	50	11	15	4	63	14	57	13	56
Firth Park	*N*	350	R	16	31	6·7	33	7·5	50	10	17	5	60	12	55	11	6
Longley	*W*	425	R	20	—	—	33	8·9	45	11	17	5	60	15	53	13	52
Central (valleys)																	
Hillsborough	*b*	225	RH	18	—	—	33	6·5	52	9	15	4	63	10	57	9	55
Langsett Road	*Z*	225	RH	32	—	—	41	9·7	58	13	17	5	67	15	63	14	51
Woodside Lane‡	*A*	275	RH	23	39	8·7	37	10·1	56	12	24	6	51	16	53	14	41
Ellesmere Road‡	*B*	225	RH	35	40	8·8	40	9·7	59	11	22	6	73	15	66	13	40
Newhall‡	*C*	125	HR	21	42	12·8	46	13·3	59	17	25	8	78	20	69	19	38
Attercliffe	*J*	150	RH	29	43	10·1	45	10·1	63	13	24	9	75	12	69	13	42
Darnall	*a*	225	RH	24	—	—	50	12·5	68	15	29	7	88	23	78	19	53
Carbrook	*f*	125	HR	14	—	—	46	15·2	—	—	28	10	72	23	65**	21**	58
Wincobank	*R*	150	H	7	27	10·2	26	12·9	43	15	14	7	46	23	45	19	48
Infirmary	*g*	210	RH	36	—	—	45	9·8	—	—	23	6	81	14	77**	12**	61
St. Stephens‡	*D*	275	R	33	37	8·1	34	9·2	53	12	20	4	52	17	53	15	37
Milton Street‡	*E*	250	LR	31	40	10·0	43	11·0	62	15	24	4	74	20	68	17	39
Surrey Street‡	*F*	280	CL	12	28	10·2	26	13·7	43	14	13	6	46	21	45	15	2
Park‡	*G*	250	LR	13	32	8·8	36	10·2	46	12	20	6	64	19	55	15	32
Royal Hospital	*h*	310	LC	19	—	—	35	10·1	—	—	16	5	67	18	63**	14**	65
Ecclesall Road	*T*	280	R	24	—	—	37	6·5	43	10	15	3	67	11	55	11	49
Sharrow‡	*H*	280	RL	46	40	7·8	46	9·6	63	12	21	4	83	18	73	15	36
Lowfield	*Q*	220	RL	36	50	8·2	51	8·5	73	13	29	5	87	14	80	13	47
Western and Southern																	
Walkley	*K*	515	R	33	30	5·7	36	8·4	43	8	18	4	57	14	50	11	62
Harcourt Road	*V*	425	R	30	—	—	31	6·5	43	7	13	3	60	12	51	9	50
Greystones	*d*	450	R	19	—	—	30	6·8	41	9	13	4	54	12	47	9	57
Nether Edge	*P*	375	R	18	21	5·4	26	6·7	34	8	12	4	50	12	42	10	46
Manor	*M*	650	R	18	24	6·1	31	7·6	38	9	15	5	59	13	49	11	44
Woodseats	*X*	400	R	18	—	—	27	6·9	34	7	14	4	54	13	39	10	54
Button Hill	*j*	500	R	4	—	—	20	3·6	—	—	7	2	44	6	35**	5**	63
Fulwood	*O*	825	R	2	8	2·1	13	2·1	11	3	4	1	23	3	17	3	64
Redmires	*e*	1000	open moor	0	—	—	6	2·3	—	—	3	1	9	4	7**	4**	60

* R = residential, H = heavy industry, L = light industry, C = commercial.
† Based on average number of electors per acre in area of ½ mile radius round site.
‡ Instruments operated by local authority.
** Based on 1958–59 only but corrected for average difference between the 2 years at neighbouring sites.

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The mean of the two winters' values is also given in Table 1 in order to provide a single index of pollution to be used in relation to elevation and population density. In the five cases where no readings were available for the first winter, an approximation was made by correcting the second winter's figures for the average difference between the two winters at neighbouring sites.

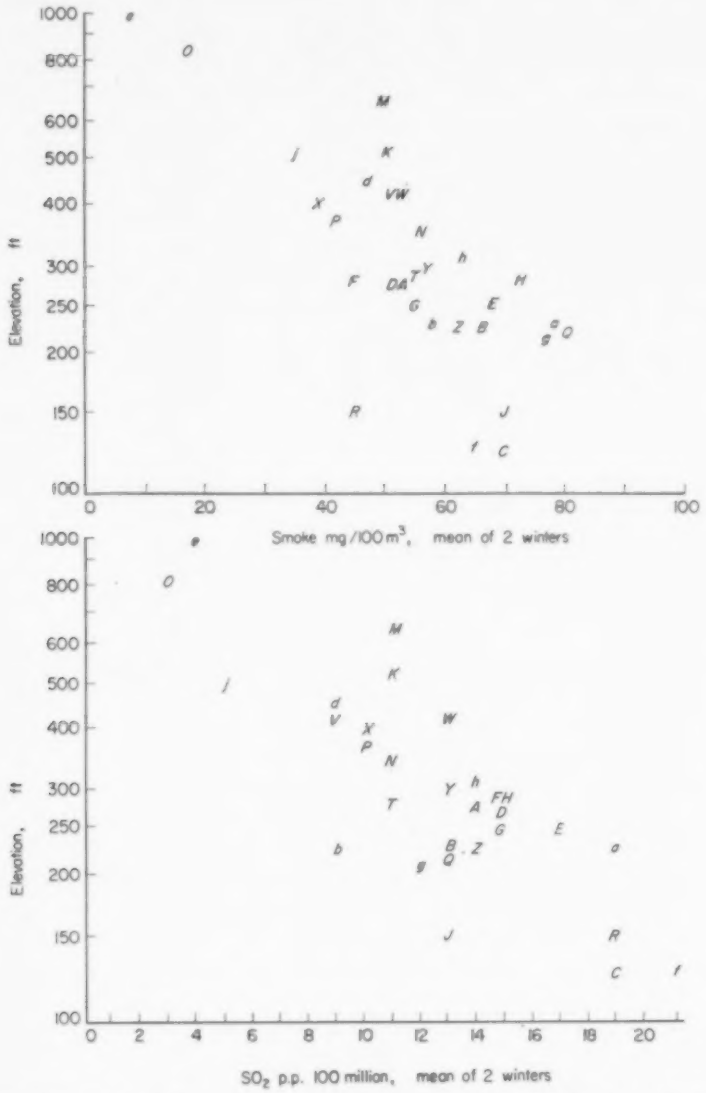

FIG. 3. Elevation and pollution. In the upper graph the elevation at the site of each pollution instrument is plotted on a logarithmic scale against the mean smoke value for two successive winters (Nov.–Jan. 1957–58 and 1958–59) at that site. The code letter for each site is used so that relevant information given in Table 1 and Fig. 1 may be considered. The lower graph shows the mean sulphur dioxide value for the same two winters in relation to elevation.

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ELEVATION AND POLLUTION

In Fig. 3 the elevation of each site (on a logarithmic scale) is plotted against smoke and against sulphur dioxide, taking the mean of the two winters readings in each case. The code letters are used on the graphs so that information about the sites given in Table 1 and Fig. 1 can be taken into consideration.

Both graphs show a decrease of pollution with height above sea level. There are several points of interest in the relative positions of certain sites on the two graphs. For instance, *R*, *f* and *C* (all in the north-eastern valley in the area of heavy industry) have high values for sulphur dioxide, but much less smoke than would be expected from the general trend of the upper graph; and the contrast is greater in the case of *R* which is purely industrial than for *f* or *C* where there are some small houses among the steel works.

In another instance, *Q* and *a* have almost identical amounts of smoke but *a* has as much sulphur dioxide as *R* and *C* whereas *Q* has less. Site *a* is in the same valley as *R* and *C* and receives sulphur dioxide from the steel works, but *Q* lies in the Sheaf valley, well away from them. Site *J* on the other hand is in the vicinity of the steel works but has no more sulphur dioxide in winter than *Q*. This might be due to the neutralization of sulphur dioxide by some alkaline effluent in the neighbourhood and it is hoped to investigate this problem.

AIR POLLUTION AND POPULATION DENSITY

Fig. 4 shows smoke and sulphur dioxide in relation to population density. Once again the mean of two winters' pollution is used. The graphs for elevation were very much alike, but this pair are quite different. The graph for smoke shows a correlation between this pollutant and the number of electors per acre in the district, but in the graph for sulphur dioxide there is no such correspondence. In this graph, sites *R*, *f*, *C* and *a* (already mentioned as being in or near the area of heavy industry) are shown as having much sulphur dioxide although the population density is low or moderate. Sites *F* and *G* also have relatively high levels of sulphur dioxide. *F* is in the business and commercial area where central heating is the rule, and *G* nearby has been the scene of much slum clearance and rebuilding.

Since even the most heavily industrialized areas do not produce more smoke than would be expected on the basis of their population, even though the sulphur dioxide levels are very high, it appears that domestic chimneys must account for the greater part of smoke pollution. Because the areas of denser population lie in the valleys in Sheffield it might be thought that this accounted for the correlation between smoke and elevation, but if an area on the hillside such as that round site *K* is considered, it can be shown that population density and elevation do in fact have separate effects. The position of site *K* in relation to others in the two graphs for smoke in Figs. 3 and 4 should be studied. In Fig. 3 site *K* has rather more smoke than would be expected for its elevation compared with site *j* with less population. In Fig. 4 on the other hand it has a good deal less smoke than other sites with the same population density, all of which are lower down.

In the valleys, air chilled by contact with higher ground flows down in calm weather to form a cold, stable mass of air within which pollution accumulates; on higher ground pollution is dispersed much more rapidly.

DISTRIBUTION OF POLLUTION: YEARLY MEANS APRIL 1958–MARCH 1959

To illustrate the distribution of pollution in Sheffield over different periods a map of the city has been drawn with a circle at the site of each instrument. The size of the circle represents the area (roughly ½ mile or 0·8 km in diameter) over which the instrument gives a reliable estimate of pollution. For monthly means the greatest error is within plus or minus 40 per cent, nineteen times out of twenty (see CLIFTON *et al.* (1959) in this issue).

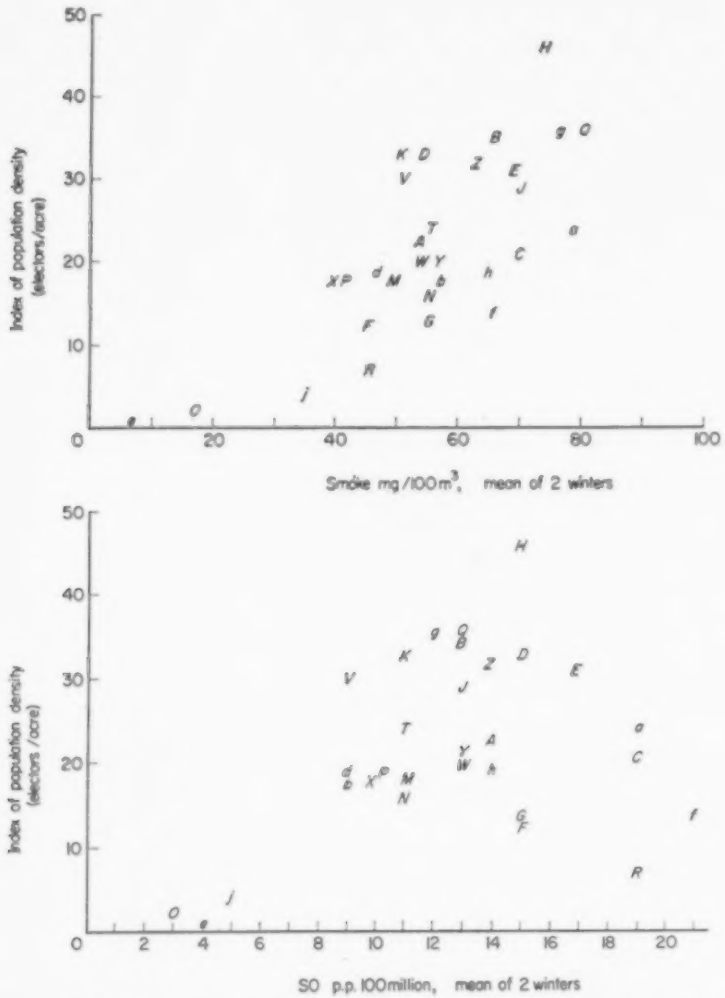
Index of population density (electors/acre)
Smoke mg/100m³, mean of 2 winters
Index of population density (electors /acre)
SO p.p. 100million, mean of 2 winters

FIG. 4. Population density and pollution. An index of population density at the site of each pollution sampling instrument was obtained by assessing the mean number of electors per acre in an area of ½ mile (0·8 km) radius round the site from the map in Fig. 2. This index was plotted against the mean smoke value for two winters for each site (as in Fig. 3) in the upper graph and against the corresponding sulphur dioxide value in the lower graph. For code letters see Table 1 and Fig. 1.

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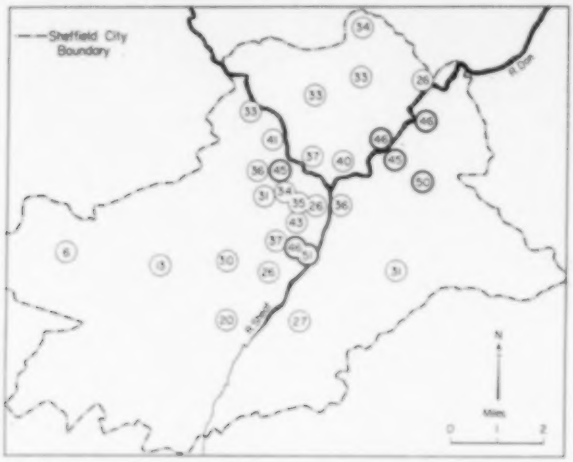

Fig. 5. Map of Sheffield showing 1 year's mean smoke values at the site of each sampling instrument. The period covered is from April 1958 to March 1959 inclusive. Heavy outlines indicate sites with heaviest smoke pollution.

The yearly means for smoke for each site from Table 1 are entered in the circles on this map in Fig. 5. They vary from 6 mg/100 m³ on the open moors 1000 ft above sea-level to 51 mg in a densely populated area with small industrial premises (site *Q*). Heavily outlined circles denote the sites with the heaviest pollution. These occur in each of the valleys and comparison with the population density map (Fig. 2) shows that they correspond with areas of dense population. In the city centre (site *F*) the smoke value is relatively low (26 mg/100 m³) and the same value is found at site *R* n the purely industrial area on the north-east.

The map in Fig. 6 shows the distribution of the same year's means for sulphur dioxide, with values ranging from 2·1 and 2·3 parts per 100 million on the west to 15·2

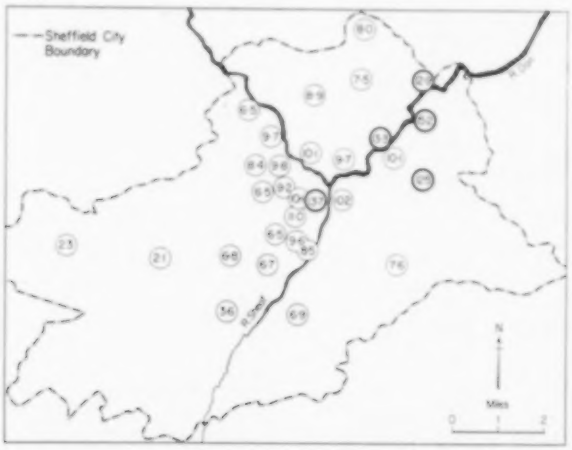

Fig. 6. Map of Sheffield showing 1 year's mean sulphur dioxide values at the site of each sampling instrument. The period covered is the same as in Fig. 5, and heavy outlines indicate sites with heaviest sulphur dioxide pollution.

parts in the north-eastern industrial valley. The heaviest concentration (denoted by the dark circles) is found in areas where there is heavy industry (sites *R*, *f* and *C*) and in the business and commercial centre (site *F*). At site *a* there is a fairly densely populated area with heavy industry nearby, and this is the only site where the sulphur dioxide and smoke values are both high. It is interesting to note that two of the sites with high sulphur dioxide levels are *F* and *R*, mentioned in the previous paragraphs as having relatively low smoke levels, one being associated with a large number of central heating installations and the other in a non-residential area with much heavy industry.

Another point of interest in comparing Figs. 5 and 6 is the fact that site *e* on the moors has slightly more sulphur dioxide than the suburban site *O*, but only about half as much smoke. This raises the question of the sources of each type of pollution and the distance which each is likely to travel. It is hoped to discuss this matter fully in a forthcoming publication dealing with the effects of the weather on pollution.

For sixteen sites the means of two successive years are available (Table 1). The smoke values are seen to be higher in 1958–59 than in the previous year except at four sites, *A*, *R*, *D* and *F*, where they decreased, and one, *B*, where they were the same. Sites *A*, *D* and *F* are in or near the newly-designated Smoke Control Area No. 1 in the city where much slum clearance has been carried out and more efficient stoking encouraged. Site *R* is almost purely industrial.

When the 2 years' means for sulphur dioxide are compared, there has been no decrease at any site; at two (*J* and *O*) the value has remained the same, and all others show an increase.

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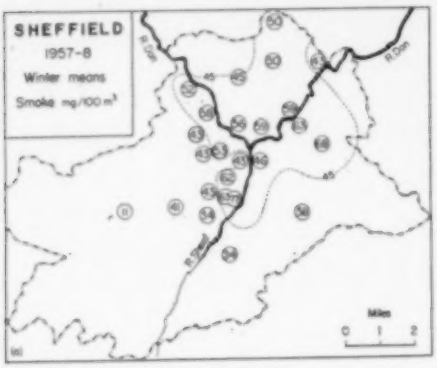
COMPARISONS BETWEEN SUMMER AND WINTER POLLUTION LEVELS

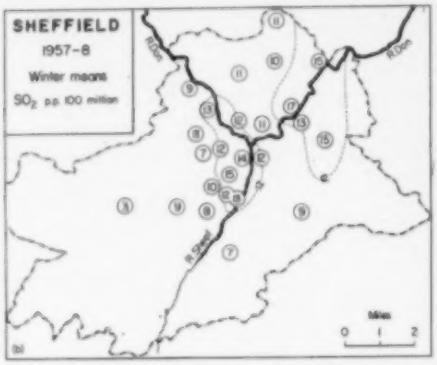
Six maps have been prepared to illustrate the winter and summer distribution of pollution. Figs. 7a and 7b show mean smoke and sulphur dioxide levels for the winter of 1957–58 (previously defined), Figs. 8a and 8b those for the summer of 1958, and Figs. 9a and 9b those for the winter of 1958–59.

In each of these six maps a broken line has been drawn to connect places with equal pollution, just as contour lines are used to connect places with equal elevation. These particular " pollution contours " were chosen because they outline similar areas in each of the three seasons. The areas differ for smoke and sulphur dioxide, but they illustrate the fact that the pollution in the summer of 1958 was less than half that of the previous winter (the summer contours for 20 mg of smoke and 6 p.p.m. of sulphur dioxide cover rather less than the previous winter's contours for 45 mg of smoke and 12 parts of sulphur dioxide). During the second winter, however, there was more pollution than in 1957–58; the corresponding smoke contour is for 60 mg and the sulphur dioxide contour for 18 parts per 100 million, or three times the summer's values over the same area. During the winter 1958–59 there were four foggy periods with high levels of pollution whereas no very severe episodes occurred in 1957–58. No conclusion can be drawn about any general trend on the evidence of two winters but the fall in smoke at sites *A* and *D* and the very small rise at *R* and *F* in the second winter, in contrast to the marked rise at all other sites, is probably of significance, as was mentioned in connexion with the yearly means.

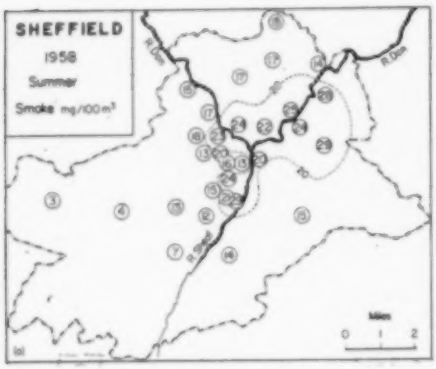
The different distribution of smoke from that of sulphur dioxide seen in these maps reinforces the impression already gained from the maps of yearly means (Figs. 5 and 6).



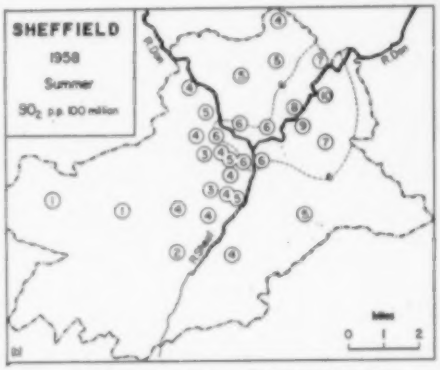
7(a) Winter 1957–58: Smoke



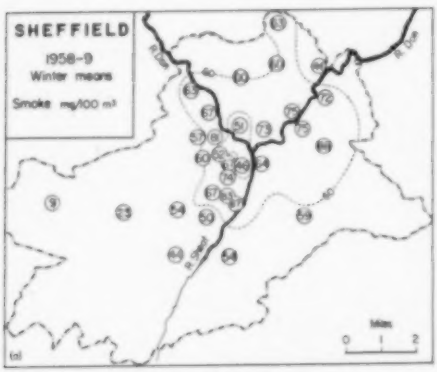
7(b) Winter 1957–58: Sulphur dioxide



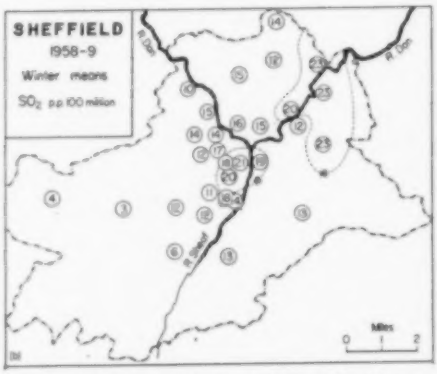
8(a) Summer 1958: Smoke



8(b) Summer 1958: Sulphur dioxide.



9(a) Winter 1958–59: Smoke



9(b) Winter 1958–59: Sulphur dioxide

FIGS. 7, 8 and 9. Map of Sheffield with mean smoke and sulphur dioxide values for 3 month periods at the site of each instrument. Winter values represent means for November, December, and January; Summer values those for June, July and August. Broken lines are pollution contours joining places with equal pollution levels.

Sulphur dioxide is chiefly associated with heavy industry and the business and commercial centre; smoke is relatively less at the city centre but is heaviest where population density is high, especially when these areas also contain small industrial premises such as characterize the older parts of Sheffield, and are situated on the floor of the valley.

Acknowledgements—The authors wish to offer sincere thanks for their co-operation throughout the study, one part of which this paper reports, to

Dr. G. NAGELSCHMIDT and his colleagues of the Safety-in-Mines Research Establishment of the Ministry of Power, Sheffield.

Dr. LLYWELYN ROBERTS, Medical Officer of Health, Sheffield, and his staff, particularly Mr. J. W. BATEY, Supt. Smoke Inspector.

Dr. MARION C. TAYLOR, until recently Principal School Medical Officer for Sheffield, and her staff.

Mr. J. SWEENEY, and his colleagues in the Sheffield branches of the Ministry of Pensions and National Insurance.

Mr. J. BARWICK, Meteorological Officer, Sheffield; his fellow-members of the Sheffield Meteorological Society; and the many other volunteer helpers who assisted the work of the Group.

Mrs. A. BATES carried out the clerical work, and Mrs. A. BARRETT and Miss M. TOOLE the coding, punching and tabulating. Mr. A. SYLVESTER was responsible for the collection and estimation of samples in the earlier stages of the investigation.

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THE RELIABILITY OF AIR POLLUTION MEASUREMENTS IN RELATION TO THE SITING OF INSTRUMENTS

MARJORIE CLIFTON, D. KERRIDGE, WINIFRED MOULDS, J. PEMBERTON* and J. K. DONOGHUE†
The Medical Research Council Group for Epidemiological Research on Respiratory Diseases (Air Pollution), University of Sheffield
(*Received* 20 *May* 1959)

Abstract—(1) A study of the reliability of air pollution measurements has been made. The results will serve as a guide to the siting of instruments and to the accuracy with which the average pollution of an area can be assessed from a given distribution of instruments.

(2) If 40 per cent in either direction is an acceptable limit of error (that is, a coefficient of variation of 20 per cent) it is necessary to have one instrument every ½ mile (0·8 km) for daily values, or every mile (1·6 km) for monthly mean values.

(3) Eight instruments are required to estimate the average pollution of Sheffield to within plus or minus 20 per cent of the values obtained by using twenty-eight instruments.

(4) A simple method of selecting sites in relation to population density is suggested.

THE main research programme of the above M.R.C. Group was to study the relationship between air pollution and respiratory disease. However, two secondary problems arose from the necessity, under ordinary conditions, of using a limited number of sampling instruments. The first was to decide the area over which a single instrument gives a fair estimate of the level of pollution, considering both daily measurements and mean values over longer periods. The second was to find the accuracy with which the average pollution of a whole town can be estimated with a given number of instruments, and to decide how the instruments should be sited to give an estimate which might be used for making valid comparisons between towns.

1. THE AREA OVER WHICH AN INSTRUMENT GIVES A RELIABLE ESTIMATE OF POLLUTION

The report on atmospheric pollution in Leicester (D.S.I.R., 1945) states that " observations in Leicester support the view that within a large uniformly populated area, but not too near its windward edge, the concentration of smoke in surface air will vary little from place to place ". In the majority of towns however observations have to be made in areas which are not uniform. To test the variation of pollution from place to place under these conditions it was decided to compare the readings from instruments sited at increasing distances from each other. No two of the instruments used for routine daily measurements were nearer together than ½ mile (see PEMBERTON *et al.* (1959) in this issue), so observations over shorter distances were made as a separate series of experiments. The district surrounding the laboratory was thought to be suitable as it included many different types of building, on sloping ground, near the centre of the city.

(a) *The accuracy of estimation of pollution by daily measurements*

The first step was to compare the readings from several instruments in the same

* Now Professor of Social and Preventive Medicine, Queen's University, Belfast.
† Now at U.K. Atomic Energy Authority, Springfields Works, Salwick.

place, and four were run out of the same window at the laboratory. This gave an estimate of the intrinsic instrumental errors (experiment *A* in Table 1). Errors which would affect all instruments in the same way, such as those inherent in the scale of shades calibration for smoke, were ignored. Another source of error in dealing with horizontal changes in pollution might have arisen from the fact that it was not always possible to place the inlet funnels at the same height above the ground, so an experiment was carried out in which samples were taken with four instruments, the inlet funnels of which were placed vertically above one another at heights of 10, 20, 30 and 40 ft (3, 6, 9 and 12 m) above ground level (experiment *B* in Table 1).

After these preliminary experiments the distance apart was increased, in stages up to 1302 yd (1191 m). In order to make direct comparisons possible the stages

FIG. 1. Map of central Sheffield showing the laboratory and other sites where instruments were placed for experiments *A* to *F* in Table 1. For experiment *C*, sites 1, 2*A*, 3*A* and 4*A* were used; for experiments *D* and *E*, nos. 5, 6 and 7; and for experiment *F*, nos. 2*B*, 3*B* and 4*B*.

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were arranged to overlap, so that pairs of experiments at different distances were being carried out at the same time. For the first pair of experiments seven instruments were set out, the central one at the laboratory and six others along three spokes radiating from it. (Fig. 1 and experiments *C* and *D* in Table 1.) Later, instruments 2*A* and 3*A* were moved out beyond 5 and 6 to sites 2*B* and 3*B*. There was already a regular daily sampling instrument suitably placed in relation to site 7, at 4*B*.

All measurements were taken using the standard volumetric instrument recommended by the Department of Scientific and Industrial Research (D.S.I.R., 1957) which samples suspended particulate matter (smoke) and gaseous sulphur dioxide. All stains were measured photoelectrically. For a more detailed description of the methods used see PEMBERTON *et al.* (1959) in this issue.

TABLE 1. COEFFICIENTS OF VARIATION OF DAILY MEASUREMENTS OF SMOKE AND SULPHUR DIOXIDE AT DIFFERENT DISTANCES

Experiment No.	Month	No. of instruments	Mean distance apart	No. of days covered	Means of daily values		Coefficient of variation (%	
					Smoke (mg/100 m³)	SO_2 (p.p. 100 m.)	Smoke	SO_2
	1957							
A	May/June	4	Same window	12	13	4·9	8	5
B	April/May	4	6 yd (5·5 m) (vertical)	16	31	8·2	6	5
C	November	4	222 yd (203 m)	22	57	15·0	9	9
D	November	3	532 yd (486 m)	22	60	15·0	19	16
	1958							
E	January	3	532 yd (486 m)	23	53	13·3	12	21
F	January	3	1302 yd (1191 m)	21	40	11·4	54	83

Discussion. The coefficients of variation in experiment *B* do not differ appreciably from those obtained in experiment *A*. It appears that the height of the sampling funnel is unimportant within the limits of the experiment, i.e. up to 40 ft above ground level in a city.

The results of experiments *A* and *B* taken together show that a coefficient of variation of about 7 per cent for smoke and 5 per cent for sulphur dioxide is inherent in the method of measurement. For comparison, the Leicester report quotes 15 per cent for smoke measurements (obtained by a slightly different technique) and 3 per cent for sulphur dioxide. The figure of 15 per cent was obtained under deliberately chosen adverse conditions: 5 per cent is quoted as the best obtainable. This Group's present figures are probably typical of ordinary running conditions.

Experiments *C* to *F* formed part of the general plan of measuring the decrease of accuracy with distance. The comparison between the results of *D* and *E* is of interest since these results were obtained with the same instruments, in the same positions, but 2 months later. Because of the marked change in the coefficient of variation, only results obtained during the same period for the different distances should be used for formal statistical assessment of variation with distance.

Comparing the results of *C* and *D* using the variance ratio test, the increases in

variability in both the smoke and sulphur dioxide measurements were found to be significant at the 1 in 1000 level. Similarly, comparing the results of experiments *E* and *F*, the increases in variability are significant, at the same level.

These results suggest that in a district of the type studied the area over which an instrument gives a reliable estimate of pollution is not very large. The coefficients of variation are of the order of 10 per cent at $\frac{1}{8}$ mile (200 m) and 20 per cent at about 500 yd or 500 m. In other words, the limits of error are 20 per cent and 40 per cent respectively in either direction. The coefficients of variation at these distances do not differ appreciably for smoke and sulphur dioxide measurements. It appears therefore that to be able to estimate the daily pollution at any point of a mixed area with even moderate accuracy, an instrument every $\frac{1}{2}$ mile (0·8 km) would be needed.

(b) *The accuracy of pollution estimates using monthly means*

The results so far discussed all refer to the reliability of daily readings. The results obtained in the course of routine pollution measurements have been used to assess the reliability of monthly means. From among the thirty instruments running in Sheffield six pairs can be selected so that the first member of each pair is $\frac{1}{2}$ mile (0·8 km) from the other. The differences between the members of these pairs give an estimate of the coefficient of variation at $\frac{1}{2}$ mile (0·8 km). The same method was used for sites at distances of 1 mile (1·6 km) and 2 miles (3·2 km).

Table 2 shows results obtained in this way based on the complete year February 1958 to January 1959 inclusive. During this period the mean pollution for the twenty-eight sites used for these calculations was 36 mg of smoke per 100 m^3, and 9·1 parts of sulphur dioxide per 100 million.

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TABLE 2. COEFFICIENTS OF VARIATION OF MONTHLY MEAN VALUES FOR SMOKE AND SULPHUR DIOXIDE AT DIFFERENT DISTANCES

Distance between sites	No. of pairs used	Coefficient of variation (%)	
		Smoke	SO_2
$\frac{1}{2}$ mile (0·8 km)	6	19	7
1 mile (1·6 km)	11	25	26
2 miles (3·2 km)	13	25	31

Discussion. At a distance of $\frac{1}{2}$ mile (0·8 km) the coefficient of variation for smoke is more than twice that for sulphur dioxide. This contrasts with the results for daily measurements, which showed roughly the same variation for both at shorter distances. The results in Table 1 however were obtained from an area which although containing a mixture of housing and light industry did not include any sharp change, either of elevation or to an area of different type. Results taken from the whole of Sheffield are influenced by the tendency for industry to be concentrated in well-defined areas, in which large amounts of sulphur dioxide are produced. The distribution of housing, responsible for much of the smoke production, is more uniform, and so the effect of the grouping of industry into areas is greatest on sulphur dioxide measurements. At a distance of $\frac{1}{2}$ mile (0·8 km) there is a reasonable chance that if one member of a pair is in an industrial area, the other will be also. At a distance of 2 miles (3·2 km) this is almost impossible, and at this distance the variation for sulphur dioxide is greater than that for smoke.

The difference between members of a pair of instruments is of course influenced by other factors, notably elevation, since pollution in Sheffield is largely produced in the valleys and is more easily dispersed from higher ground. It follows that to obtain the most accurate results with a given number of instruments it is advisable to place them close together where sharp changes in elevation or type of district occur, even at the expense of having them more widely spaced where conditions are uniform.

2. THE AVERAGE POLLUTION OF SHEFFIELD

By the " average " pollution of a city we mean in this context the average pollution to which the population is exposed. This point is important, since within the Sheffield city boundary, for instance, there are several square miles of open moorland. If the sites of sampling instruments were evenly spaced over the whole area of the city it would be necessary to weight the reading at each site by the population density in the area surrounding it.

If the normal practice of using the arithmetic mean of the results is to be retained, the sites must be closer together in areas of high population density in order to give a fair picture of pollution as it affects the inhabitants. This method also has the theoretical advantage that the estimate has a lower coefficient of variation.

Table 3 shows the error in estimating the average pollution of Sheffield (that is, the mean of all instruments) from the mean of any eight instruments chosen at random. Eight was chosen as the number likely to be running under normal circumstances in a city the size of Sheffield. It was in fact the number running in Sheffield before the M.R.C. Research Group was set up. (The error of estimate for the mean of n instruments may be obtained by multiplying each coefficient of variation in the table by $\sqrt{\frac{8}{n}}$.) In practice, the sampling would not be random; for instance we might specify that four of the eight sites must be in the valley, and four above. The result of making this restriction is shown in the last line of the table.

TABLE 3. COEFFICIENTS OF VARIATION OF THE MEAN OF EIGHT INSTRUMENTS AS AN ESTIMATE OF THE AVERAGE POLLUTION OF SHEFFIELD OVER DIFFERENT PERIODS

Period	Mean values, 28 sites		Coefficient of variation (%) Mean of eight instruments	
	Smoke (mg/100 m³)	SO_2 (p.p. 100 m.)	Smoke	SO_2
July 1958	16	5·0	13	16
September 1958	19	5·4	11	12
November 1958	64	15·8	8	12
Year ending January 1959	36	9·1	8	11
Same, but four below 280 ft and four above	"	"	10	14

Discussion

From Table 3 it is clear that a coefficient of variation of the order of 10 per cent or more must be expected in estimating the pollution of Sheffield from the mean of eight

sites; in other words, the difference of the true value from the estimate will be less than 20 per cent in either direction, nineteen times out of twenty. There are some theoretical objections to using random sampling theory when the values at neighbouring sites are not completely independent, and the error which could arise from this cause would tend to exaggerate the coefficients of variation. However, in the case of smoke the maximum variability has already been reached at a distance of 1 mile (1·6 km) so the error will be small.

The greater variability in summer is probably due to the greater amount of turbulence in the atmosphere causing more rapid dispersal of pollution. In winter, when dispersal is poor, there is more opportunity for mixing to take place, so that pollution produced in one part of the city affects results in another.

3. THE SITING OF AIR POLLUTION INSTRUMENTS

An ideal method of distributing air pollution sampling instruments in a city to get the most accurate estimate of the average pollution to which the inhabitants are exposed would be very laborious, quite apart from the fact that the mathematical theory of such sampling has not yet been worked out.

At present the selection of sites in different towns is made on a variety of grounds; for this reason no comparison of air pollution figures between towns is very reliable. If some consistent method of siting instruments were used, then there would be a better basis for comparing air pollution statistics, so that their relationship to health might be studied more effectively.

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The method suggested here, although not ideal, does offer a simple, practicable solution to the problem of selecting sites which could be applied in any town.

The method is as follows:

From a map on which the electoral polling districts are outlined, the surface area of each district is ascertained by means of a planimeter, in square inches. The acreage of each polling district is calculated by dividing the total acreage of an electoral ward (which is already known) among its constituent polling districts in proportion to the number of square inches of map surface in each as measured by the planimeter.

Using the list of polling districts published by the local authority, the number of electors in each is divided by the number of acres, giving a figure of *electors per acre*. This serves quite satisfactorily as an index of population density because the ratio of electors to total population varies relatively little.

A list of polling districts is next prepared in which they are arranged in descending order of population density. In a second column is written the actual number of electors, and in a third these are added successively to give cumulative totals of electors. From this list the choice is made of the polling districts within which instruments are to be sited. The method must be modified where only very few instruments are available, in order to avoid sampling the extremes of heavy and light pollution, but in general, where six or more sets are used, the selection of a site is made by using random numbers in the following way:

Using random number tables to the same number of digits as the total number of electors, numbers are taken in order as they occur. The polling district with the cumulative total next above the random number is chosen, and one instrument is to be placed in this district unless its boundary touches at any point a polling district already chosen. In this case the next random number is used. The actual choice of site will

depend on local circumstances, but the neighbourhood of any localized heavy source of pollution should be avoided. If for practical reasons no site can be found in the polling district chosen, the nearest convenient site should be used, but this must not be in a polling district with a greatly different population density; in other words, it must lie in a district from the same part of the list.

The possibility arises that when there is no suitable site in the chosen district, the nearest site in a similar type of district may fall in a district adjacent to one already chosen, and hence too near another instrument. In such a case a fresh random number should be taken.

The modification for the choice of sites numbering less than six involves cutting off from the top and bottom of the list of polling districts a certain proportion of the population (arbitrarily decided) and making the choice only from the middle range. Since pollution is related to population density this is a way of avoiding the very heavily or very lightly polluted areas without introducing a bias.

For one instrument, the total number of electors is divided by three; the cumulative total nearest to the figure of one-third of the electors is marked and a line drawn below it; then the cumulative total nearest to the figure of two-thirds of the electors is marked and a line drawn below that. From the polling districts between the lines, one is chosen by random number as described above. If there is no convenient site there, the nearest may be selected as long as the polling district concerned lies between the two lines on the list.

For two instruments the lines are drawn below the polling districts with cumulative totals nearest to one-quarter and three-quarters of the total of electors; for three instruments the fractions are one-sixth and five-sixths; for four instruments, one-eighth and seven-eighths; and for five instruments, one-tenth and nine-tenths. The same rules as before apply to districts adjacent to those already chosen.

It was mentioned above that the use of eight instruments to assess the average pollution of a city gives results within limits of error of about 20 per cent (Table 3). Using the formula provided, the figure of six instruments is found to be about 25 per cent, but for three is only about 36 per cent, for two 44 per cent, and for one 62 per cent (57 per cent for smoke and 68 per cent for sulphur dioxide). The variations between cities will often be less than this, so one or two instruments will not give reliable information as to the relative average pollution to which the inhabitants of different cities are exposed. However, the method suggested here offers a slight improvement over a purely random choice in that it selects conditions experienced by that part of the population in the middle range of population density for each of the cities concerned, whatever this may be.

It is emphasized that siting by this method is not intended to discover the *distribution* of air pollution within a city, but to determine the average levels to which the *population* is exposed. The larger the number of instruments, the more closely the realization of both aims will be achieved. It is felt that with the small numbers of instruments usually envisaged the present proposal is fairly realistic and would enable comparisons to be made which are at present invalid, because of the absence of any uniformity in the choice of sites.

Being based on population density, it is concerned with the most important aspect of air pollution: its impact on the inhabitants. Choosing the districts by random numbers ensures that the sampling is in proportion to population, since the ratio of

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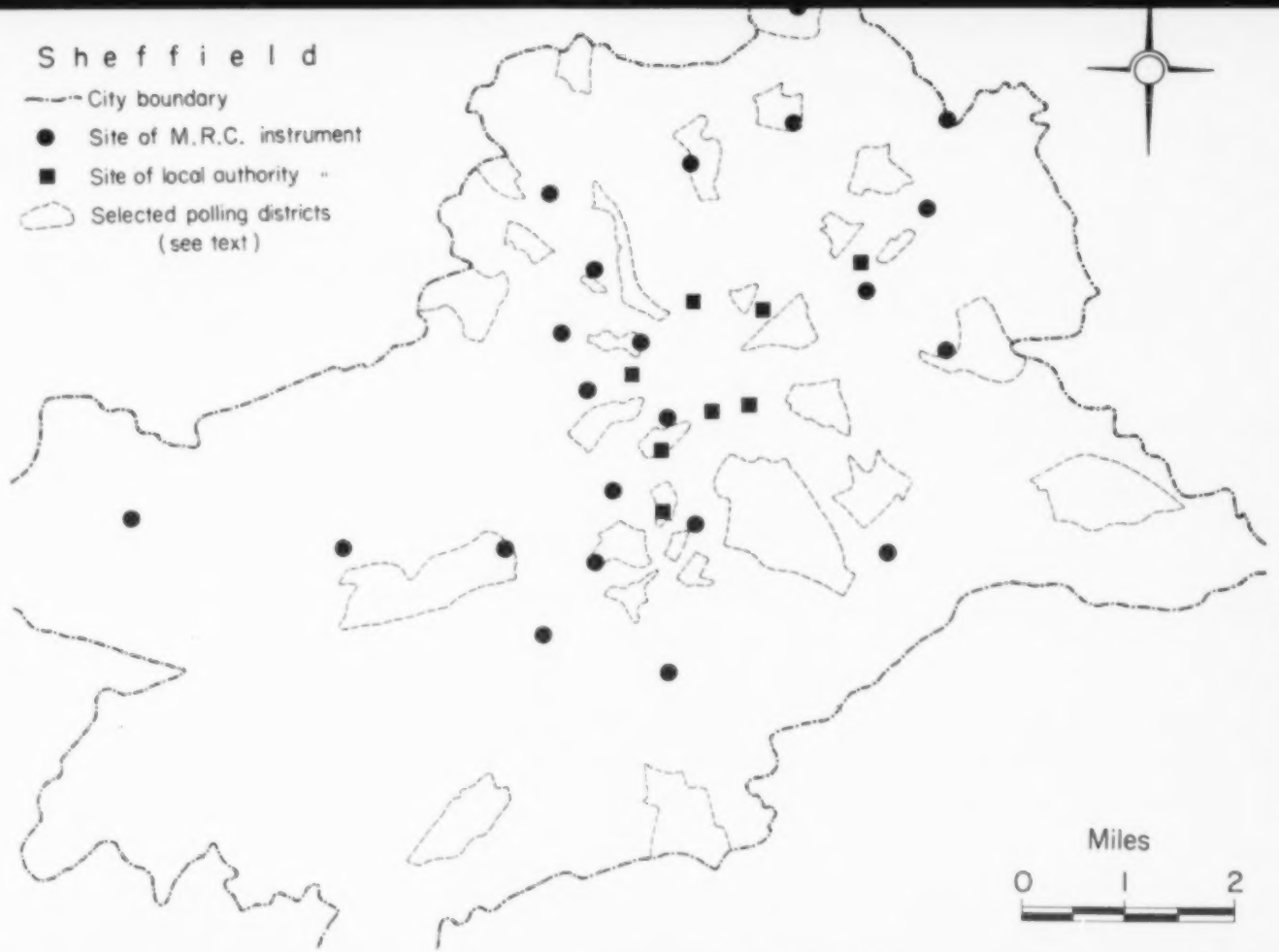

FIG. 2. Map of Sheffield showing sites of daily pollution sampling instruments. Eight indicated by squares were already operated by the local authority prior to the setting up of the M.R.C. Group by whom the others (shown as circles) were installed. The areas enclosed by narrow black lines are electoral polling districts selected by means of random numbers (see text). Instruments, if placed one in each of these areas, would be sited in relation to population density.

electors to total population is sufficiently constant for this purpose. Avoiding any district which touches one already chosen means that sites will be spread out fairly evenly. A slightly more accurate rule would be to specify a minimum distance between sites proportional to the square root of the population density, but as the size of polling districts is on the average related inversely to population density, the simpler rule given here achieves the same result.

The method has the practical advantage that new sites can be added without re-arranging those already in position, as would be necessary with an ideal non-random method. The application of this method of selecting electoral polling districts for the siting of instruments is shown for Sheffield in Fig. 2 which also shows the sites which were chosen on other grounds for the existing instruments. The method of selecting sites described here has a slight bias towards choosing districts near the city boundary, but this will only have an appreciable effect when the number of sites is large.

Acknowledgements—The authors wish to offer sincere thanks for their co-operation throughout the study, one part of which this paper reports, to

Dr. G. NAGELSCHMIDT and his colleagues of the Safety-in-Mines Research Establishment of the Ministry of Power, Sheffield.

Dr. LLYWELYN ROBERTS, Medical Officer of Health, Sheffield, and his staff, particularly Mr. J. W. BATEY, Supt. Smoke Inspector.

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Int. J. Air Poll. Pergamon Press 1959. Vol. 2, p. 197. Printed in Great Britain.

Notes and News

The Microscopic Identification of Particulate Dusts

On 1 May 1959 official approval was received from the Public Health Service to begin a study of common particulate matter found in the air. The objective of this program is to furnish an analytical scheme for the characterization and identification of air-borne dust particles with the microscope.

Suspended and settled dusts found as air pollutants can be identified by various chemical and physical tests, many of them time consuming or requiring very expensive equipment and not generally in the reach of budgets of municipal air pollution control departments. Many times the required tests for identification are scattered in the literature, making an orderly stepwise analysis of an unknown dust sample, difficult, if not impossible.

In bacteriology, bacteria are broadly identified by their individual shapes and size; in cytology cells are characterized by their morphology; in pathology diseased tissue has its own visible characteristics under the microscope as compared to healthy tissue; in metallography, we identify metals and alloys by their grain structure and appearance. Thus, the morphological characterization of particulate dusts by means of the microscope is the application of a well-known tool and technique to a new problem.

In general, particulates can be divided into three categories, combustion products such as soot and flyash, industrial dusts such as metal grindings, paint spray and abrasives, and finally wind generated dusts such as sand, clay, paper fibers and coal dust. Such a classification includes about 95 per cent of all suspended and settled dust found in large cities. Our study will be conducted in the Chicago area, sampling as many sources as possible in the time permitted for the program. We do hope, however, to accumulate as many other samples as possible of known particulate matter from sources outside Chicago and in this, we ask your help. Samples should please be sent to the Walter C. McCrone Associates, 501 East 32nd Street, Chicago 16, Illinois, U.S.A.

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It is our belief that members and friends of the Air Pollution Control Association have samples of particulate matter which would be a valuable contribution to the study. We are looking for dusts in the three categories of (a) combustion products, (b) industrial dusts and finally, (c) wind generated dust. It will be necessary to have a history on the sample, so that collection conditions can be defined and possible morphology differences between similar samples be accounted for.

It is hoped that the analytical scheme developed will be primarily an atlas of photomicrographs—black and white, color and stereo—providing simple recognition features that a laboratory technician can use efficiently after a few weeks of training. Morphological characteristics of each dust type will be noted and confirmatory tests, as necessary, will be included. These confirmatory tests will be held to a minimum and then only involve such measurements as refractive index and birefringence to maintain the goal of this program—a simple analytical scheme for the laboratory technician for dust identification. It is also contemplated, as one of our staff suggested, to build up a library of prepared slides of these pollutants to further aid in the analysis of dust samples.

Marvin A. Salzenstein

Int. J. Air Poll. Pergamon Press 1959. Vol. 2, p. 198. Printed in Great Britain

Book Reviews

W. L. FAITH: **Air Pollution Control.** John Wiley, New York; Chapman and Hall, London, 1959. vii × 259 pp. $8.50.

DR. FAITH's monograph is stated to be aimed at the non-technical reader or the technical non-specialist in air pollution. This is a commendable effort, since there exists no volume, at least in the United States, with this avowed purpose. It is perhaps not too surprising that the book fails somewhat in this respect. It is the almost invariable failing of books by the specialist for the general public that they suffer from alternate lapses into over-simplification and over-technicality. For example, the discussion of lapse rate and associated dispersion conditions is simplified to the point of being misleading. It would be novel to read a popular discussion of air pollution meteorology which did not give the impression that inversions were uniquely evil in causing pollution. On the other hand, the discussion of the thermodynamics of combustion is almost certainly complex beyond the abilities of the general reader. Certainly the diagram of a " backyard incinerator " on page 75, complete with thermocouples and hood should confuse even the technically trained.

The book is divided into nine chapters, comprising a general statement of " The Air Pollution Problem ", followed by chapters on meteorology; smoke; dusts, fumes and mists; gases; odors; automobile exhaust; the air pollution survey; and legal aspects. An appendix contains a lengthy table of conversion factors which will be of considerable use only to workers in the field and not to " civic betterment groups," to whom the volume is addressed. There is a substantial index.

One objection which can be raised is the extensive use of the word " smog ", which is defined as being synonymous with air pollution. This certainly will not serve to clarify for the general reader a recent newspaper headline which stated, somewhat inanely, that a certain city had " air pollution, but no smog." It would perhaps have been preferable to avoid the use of " smog " altogether, in the interest of educating the public to proper terminology.

There are a few obvious omissions in text content; specifically, in the discussion of automobile exhaust, the question of control of fuel composition as a means of modifying engine exhaust is never mentioned. While it is certainly true that this matter is controversial at the moment, it has achieved sufficient prominence in the public eye to deserve a passing mention.

The chapter on the air pollution survey seems oddly unsatisfying. In the first place, no consideration is given to the large area survey, frequently made purely by informal interviews, which can give a rapid and generally useful picture of air pollution in an area as large as an entire state. While this type of survey unquestionably does not yield as precise information as the highly instrumented attack which Dr. FAITH advocates, it is also considerably cheaper and more rapid, and yields information at least as extensive in proportion to its cost. Possibly the least satisfactory feature of this chapter, however, is the lack of any obvious philosophical justification of the survey on the various scales on which it may be attempted. Too frequently a very cursory or restricted survey is expected to yield results of far greater precision than is possible from such limited data; on the other hand, very extensive and expensive surveys are occasionally conducted in areas which warrant far less attention. A truly coherent picture of the relationship of the techniques and scale of the survey to the desired answers could have done much to educate both the public and the technical personnel of the local areas to the relationship between cost and results in such an endeavor. It may be added parenthetically that the brief glossary of statistical terms included in this chapter should either have been limited only to terms clearly definable or should have been omitted.

The above comment is intended neither to deride the purpose of the book nor to claim that it will fail utterly in its aim. Certainly an attempt to put into the hands of the public a picture of what is possible in the way of air pollution control, what is still to come, and what must be lived with, is highly commendable.

JAMES P. LODGE

PAPERS ACCEPTED FOR PUBLICATION

N. A. RENZETTI and GEORGE J. DOYLE: Photochemical aerosol formation in sulfur dioxide–hydrocarbon systems.

HERBERT E. STOKINGER: Toxicological interactions of mixtures of air pollutants. Review of recent developments.

L. DUBOIS, ANN CORKERY and J. L. MONKMAN: The chromatography of polycyclic hydrocarbons.

H. MAYRSOHN and P. P. MADER: Polarographic properties of smog aerosols.

P. J. MEADE: The estimation of ground level concentrations from an elevated source.

JAMES P. LODGE Jr., GEORGE S. BIEN and HANS E. SUESS: The carbon-14 content of urban airborne particulate matter.

HANS L. FALK, PAUL KOTIN and ADELE MILLER: Aromatic polycyclic hydrocarbons in polluted air as indicators of carcinogenic hazards.

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Int. J. Air Poll. Pergamon Press 1960. Vol. 2, pp. 201–209. Printed in Great Britain.

SYMPOSIUM ON POLYCYCLIC HYDROCARBONS

These papers were presented at the Air Pollution Symposium, 136th National Meeting, American Chemical Society, Atlantic City, New Jersey, 17 September 1959, and are published here with the kind co-operation of the American Chemical Society.

AROMATIC POLYCYCLIC HYDROCARBONS IN POLLUTED AIR AS INDICATORS OF CARCINOGENIC HAZARDS

HANS L. FALK, PAUL KOTIN and ADELE MILLER
Department of Pathology, School of Medicine,
University of Southern California
(*Received* 19 *October* 1959)

Abstract—Biological assay is the best method for evaluating the carcinogenic risk involved in breathing polluted air ; yet the lengthy procedure and other factors involved preclude its use. Consequently, the concentration of 3, 4-benzpyrene in air samples is used as an indicator of carcinogenic risks, and rapid and reliable methods for the determination of benzpyrene have been worked out. There remain, however, two obvious shortcomings in this approach.

First, polluted air frequently contains substances other than the polycyclic aromatic hydrocarbons which will produce cancer. Second, there is no accounting for other effects of polluted air. These effects, although not carcinogenic, may enhance the carcinogenic process by inhibiting the normal physiologic process by which foreign materials are eliminated from the lung. The slowing and cessation of the mucous flow in the lung are the result of inhalation of irritants such as automobile exhaust.

The conditions under which quantitation of 3, 4-benzpyrene in air samples are carried out in the laboratory may be far different from those existing in the lung.

Soot is one major source of 3, 4-benzpyrene while rubber tire dust is another. The liberation of benzpyrene from rubber tire dust by an aqueous protein solution, as is encountered in the lung, occurs rapidly. In the case of soots, particle size plays an important role in determining whether elution of polycyclic aromatic hydrocarbons will take place. Benzene, commonly used in the laboratory to extract benzpyrene from soot, will elute hydrocarbons from particles down to 40 mμ average diameter while a protein medium will be effective only with particles larger than 100 mμ diameter. The smaller particles that retain their hydrocarbons may also adsorb additional hydrocarbons that have been eluted from larger size particles in the immediate neighborhood.

Competitive effects have been observed between aromatic polycyclic hydrocarbons as found on soot and dust with regard to the production of tumors. As there is marked structural similarity between cancer-producing and inactive compounds, the intracellular site of action may be common for both groups and the latter may thus inhibit the action of the former in producing cancer. It has been shown that the contact of the two competitors with the host cell does not have to be simultaneous but that 48 hr after contact with the carcinogen, the noncarcinogen can still inhibit tumor development.

Thus, it is apparent that a chemical method for the evaluation of the carcinogenic potency of polluted air requires determination of all polycyclic aromatic hydrocarbons elutable by protein solutions. There are still a number of unidentified hydrocarbons present, as well as a number of quinonoid and phenolic derivatives of polycyclic hydrocarbons, that must be tested for carcinogenic potency and subsequently for inhibitory activity as even weak carcinogens may act as inhibitors. To complete the picture, the stability of these compounds adsorbed on soot when exposed to the atmosphere differs from one compound to the next. This instability changes the ratio of inhibitor to carcinogen by reducing the concentration of the inhibitor.

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URBAN inhabitants are exposed to a great variety of chemical agents in polluted air. Many of these have proven carcinogenic properties while numerous others because of either chemical structure or epidemiological associations are now under active investigation. It is reasonable to speculate that a large number of incompletely or wholly unidentified chemical agents exist which are in need of bioassay for carcinogenic properties. To date, only the aromatic polycyclic hydrocarbons have been thoroughly studied from the viewpoint of their carcinogenic properties. These represent a small fraction of the chemical agents present in polluted air. The purpose of this presentation is to comment upon several of the important factors which must be considered in evaluating the carcinogenic hazards existing incidental to polluted air.

The most ubiquitous and potent known carcinogenic agent in polluted air is the aromatic polycyclic hydrocarbon, 3, 4-benzpyrene. Its presence has been reported for decades, and it has been detected in all urban communities where it has been sought. Its primary source is the effluent from the incomplete combustion of solid, liquid and gaseous fuels. A secondary source is rubber tire dust. On this basis, spectrophotometric determination of 3, 4-benzpyrene in contaminated air is perhaps the most adequate measure of any existing carcinogenic hazard. Ideally, the chemical identification of this compound should be paralleled by carcinogenic bioassay of identical samples. The quantitation of 3, 4-benzpyrene represents the most desirable technique for assaying the carcinogenic hazard. Its use is more satisfactory than is either the measurement of soot fall or the determination of other aromatic polycyclic hydrocarbons as, for example, pyrene. Nevertheless, the use of benzpyrene alone falls far short of being ideal for this purpose. There are several reasons for this.

(1) Carcinogenic properties have been demonstrated in samples of polluted atmosphere free of aromatic polycyclic compounds. Certain carcinogenic fractions contain aliphatic hydrocarbons while others include oxygenated neutral compounds. In our laboratory, carcinogenic fractions have been obtained by reacting gasoline vapors with ozone (KOTIN and FALK, 1956a, 1956b ; KOTIN *et al.*, 1958). The products of this reaction are essentially similar to those occurring in certain types of polluted air. These products include, certainly among many other compounds, epoxides which have been shown by bioassay methods to be carcinogenic for experimental animals (HENDRY *et al.*, 1951 ; MCCAMMON *et al.*, 1957 ; ROSS, 1953).

(2) The hydrocarbons other than the aromatic polycyclics have in addition to their carcinogenic properties the capability of reacting with oxides of nitrogen in the presence of sunlight to produce powerful biological irritants. In addition to being recovered from the air, the hydrocarbons are demonstrable in vehicular exhausts and certain industrial effluents. The effect of the irritants formed from the hydrocarbons on the respiratory tract must certainly be considered as a factor in the development of lung cancer. Normally, all foreign matter deposited on the tracheo-bronchial tree is removed by means of the constant flow of the mucus covering the lining cells. This is accomplished by the constant beating of the cilia or whip-like threads which move constantly in the direction of the head so that the foreign matter may be either swallowed or expectorated. The irritants described are capable of interfering with ciliary action and modifying mucous secretion so that particulate matter may accumulate on the cells lining the lung (Fig. 1). This interference may vary from a marked slowing of the flow of the mucous stream with ultimate recovery following removal of the irritant, to complete inhibition or cessation of movement so that

prolonged particle retention can result (TREMER *et al.*, 1959). Repeated or extensive exposure to the irritants present in polluted air may actually result in the destruction of the superficial cells so that the underlying layer of generative cells is stimulated to multiply with the view of repairing the break in the normal lining. This is hazardous for two reasons. First, the desquamation of the superficial cells permits direct

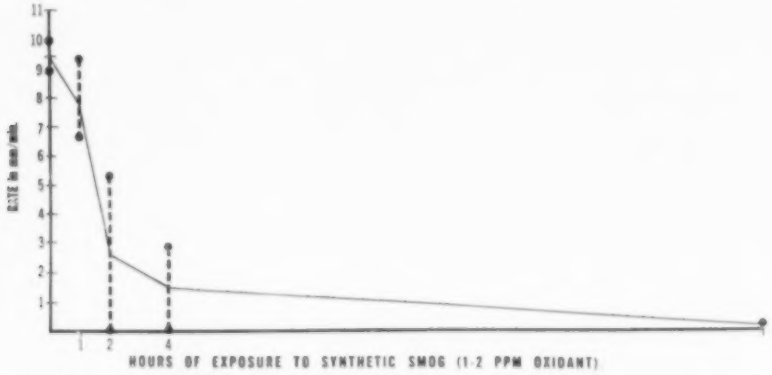

FIG. 1. The decrease in the rate of mucous movement over the respiratory epithelium of rabbits exposed to synthetic smog.

apposition of the precipitated carcinogenic particulates to the basal or generative layer of cells where presumably cancerization occurs, and second, repeated cycles of destruction and multiplication of cells provide a stimulus which, in the presence of carcinogenic agents, may serve to prepare the area for cancer development.

In urban areas where simultaneous exposure to vehicular exhausts, industrial effluents, and soot occurs, one may properly anticipate the abnormal retention of carcinogenic particulates in the lung where they may remain for sufficiently long periods for biological effects to occur. These will be described. In those areas where soot alone represents the primary source of carcinogenic air pollutants, the flow of these deposited particulates in the direction of the head with ultimate passage into the gastrointestinal tract, one must consider the possibility of a hazard in the alimentary tract.

(3) Particle size distribution studies of soot particles from vehicular exhausts show that by far the majority of particles reside within the range which is capable of entry into the lungs and retention during periods of interference with the flow of the mucous stream (DAUTREBANDE *et al.*, 1957 ; LANDAHL *et al.*, 1951). Soots of extremely small particle size (10–80 mμ) may also be retained.

The conditions under which quantitation of 3, 4-benzpyrene in air samples are carried out in the laboratory may be very different from those existing in the lung. Benzene, commonly used for such extractions, will elute hydrocarbons from particles down to 40 mμ average diameter while a protein medium will be effective only with particles larger than 100 mμ. The smaller particles that retain their hydrocarbons may also adsorb additional hydrocarbons that have been eluted from larger size particles in the immediate neighborhood. Thus, the readsorption of freed benzpyrene from the protein medium by small soot particles could be demonstrated. Other hydrocarbons present at the same time will, however, influence the degree of such

readsorption, e.g. the presence of fluoranthene in the medium will decrease the adsorption of benzpyrene due to its preferential adsorption to such particles (Table 1).

(4) A significant portion of soot particles which have been inhaled and retained in the lungs will be engulfed by phagocytes normally present in the lung. These engulfed particles become intimately associated with both cytoplasmic proteins and ultimately

TABLE 1. THE INFLUENCE OF PARTICLE SIZE OF SOOTS ON THE ADSORPTION OR ELUTION OF 3,4-BENZPYRENE FROM BENZENE AND DILUTE PROTEIN SOLUTION

No.	Soot—5 mg particle size (mμ)	3 ml Plasma solution			3 ml Benzene solution		
		BP* (μg)	% Adsorbed	BP eluted	BP (μg)	% Adsorbed	BP eluted
1	10	10	80	–	10	100	–
2	14	10	93	–	10	100	–
3	17	10	90	–	10	98	–
4	25	10	84	–	2·5	88	–
5	29	10	85	–	2·5	84	–
6	32	10	89	–	2·5	86	–
7	39	10	89	–	2·5	72	–
8	50	6	84	–			+
9	60	4	68	–			+
10	80	10	75	–			+
11	180			+			+
12	470			+			+
Diesel soot				+			+
Gasoline engine soot				+			+

* 3,4-Benzpyrene. – = No benzpyrene eluted. + = Benzpyrene eluted.

plasma proteins following liberation from the phagocytes. We have already described the marked rapidity with which aromatic polycyclic hydrocarbons may be eluted from soot particles following contact with plasma or other protein solutions. While the rate of elution varies slightly for the different aromatic polycyclic hydrocarbons, nearly all of the hydrocarbons are removed from soot particles of appropriate size following a period of 1 to 2 hr of exposure (FALK *et al.*, 1958 ; KOTIN, 1959 ; KOTIN *et al.*, 1958) (Fig. 2). At this time, the soot itself is no longer of carcinogenic significance but rather the freed carcinogenic aromatic polycyclic hydrocarbons are, as for example, benzpyrene and other compounds which are now capable of direct epithelial cell entry and presumed biological activity.

(5) Within the recent past, there has been an increasing awareness that meaningful amounts of benzpyrene are liberated into the air incidental to the wear and tear and normal degradation of rubber tires. Although the composition of the aromatic polycyclic hydrocarbons in rubber tire soot is essentially similar to the soot obtained from other sources (FALK *et al.*, 1951), the modifying effect of the rubber particles was investigated in the following manner.

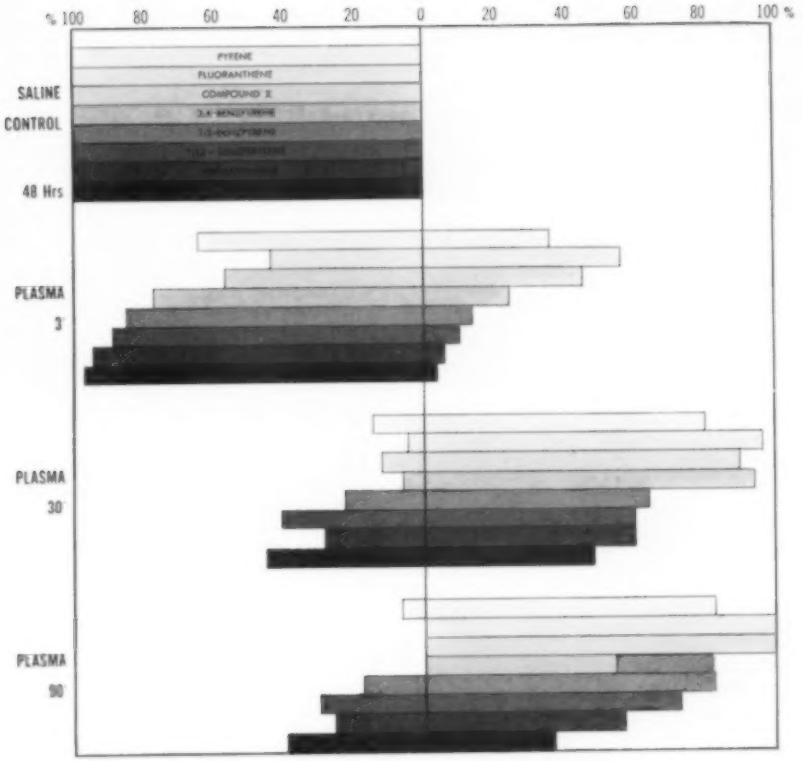

FIG. 2. The elution of polycyclic aromatic hydrocarbons from soot by plasma.
The shaded portions—from light to dark—refer to

PYRENE
FLUORANTHENE
COMPOUND X
3: 4-BENZPYRENE
1: 2-BENZPYRENE
1: 12-BENZPERYLENE
ANTHANTHRENE
CORONENE

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One hundred milligrams of rubber tire dust were placed in contact with 1 ml of plasma and the solution was shaken for 30 min at room temperature. The suspension was then centrifuged, the dust removed, and acetone was added to precipitate the proteins and extract the polycyclics. The acetone extract was reduced in volume under nitrogen and repeatedly extracted with ether. The ether extracts were evaporated, redissolved in petroleum ether and chromatographed on a column of alumina which was slightly deactivated by the addition of 2 per cent water. The chromatogram was developed with petroleum ether and all of the compounds eluted were analyzed by fluorescence spectroscopy and ultraviolet absorption spectroscopy. As can be seen, the elution of benzpyrene from rubber dust was very rapid (Table 2).

TABLE 2. EXTRACTION OF RUBBER DUST (500 mg) BY HUMAN SERUM (5 ml) ON 30 min CONTACT AT ROOM TEMPERATURE OR EXHAUSTIVE BENZENE EXTRACTION

Compound	Benzene extraction (μg)	Plasma extract (μg)	% of Total
Anthracene	10·7	3·1	29
Pyrene	29·2	4·6	16
1,2-Benzpyrene	10·2	1·0	10
3,4-Benzpyrene	15·8	4·1	26
11,12-Benzfluoranthene	+	–	0
1,12-Benzperylene	+	–	0

– = No benzpyrene eluted.
+ = Benzpyrene eluted.

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There are certain inherent problems in evaluating the carcinogenic potency of polluted air. The first and perhaps most significant of these is the competitive effect of the various compounds present in polluted air. It is well known that the various aromatic polycyclic hydrocarbons, independent of any carcinogenic properties they may have, are capable of entry into the visceral cells of the organ systems in the body (CALCUTT, 1958 ; FALK *et al.*, 1959 ; HADLER *et al.*, 1957 ; WOODHOUSE, 1954). Inasmuch as there is marked structural similarity between several of the carcinogenic aromatic polycyclic hydrocarbons and the noncarcinogenic, their intracellular site of localization, that is the receptors within the cell, may be common to representatives from each of the two groups. This may be experimentally demonstrated by the observation that a number of noncarcinogenic aromatic polycyclic hydrocarbons have been demonstrated to reduce the carcinogenic potency of strong carcinogens to the point of obliterating all carcinogenic potency at times. In our laboratory, we have demonstrated that ratios of inactive to active compounds varying from 5 : 1 to 15 : 1 resulted in a diminution in potency of the carcinogenic compound (Table 3). In other experiments in which a weak carcinogen was administered simultaneously with a potent carcinogen, very frequently the tumor yield was that which would be anticipated from the weak carcinogen rather than from the potent one. We have extended our studies to show that the simultaneous administration of these two types of chemicals to experimental animals is not critical in that the inhibitor, be it a noncarcinogen or a weak carcinogen, can be administered as much as 48 to 96 hr after the potent carcinogen with complete inhibition of the effect of the latter (CRABTREE, 1940 ; HIEGER, 1936 ; HILL *et al.*, 1950 ; KOTIN *et al.*, 1956 ; LACASSAGNE *et al.*,

TABLE 3. INHIBITION OF CARCINOGENIC ACTIVITY OF 1,2,5,6-DIBENZANTHRACENE BY RELATED COMPOUNDS ON SUBCUTANEOUS INJECTION INTO 30 MICE

Carcinogen-a dose (μg)	Inhibitor-b compounds	Dose (μg)	Molar-ratio b : a	Interval between injections a & b (days)	% Inhibition	Tumor yield compared to control
20	1,2-BA*	5000	250 : 1	0	70	11/28***
30	$(H)_2$-DBA†	450	15 : 1	0	100	0/7
60	,,	900	15 : 1	0	86	1/7
60	,,	900	15 : 1	1	72	2/7
60	,,	900	15 : 1	2	86	1/7
60	,,	900	15 : 1	4	86	1/7
30	$(H)_6$-DBA‡	450	15 : 1	0	100	0/7
60	,,	900	15 : 1	0	100	0/7
60	,,	900	15 : 1	1	100	0/7
60	,,	900	15 : 1	2	100	0/7
60	,,	900	15 : 1	4	86	1/7
275	Phen.**	2069	12 : 1	0	0	10/10
275	,,	4125	24 : 1	0	30	7/10
275	,,	8250	48 : 1	0	60	4/10

* 1,2-Benzanthracene.
† Dihydro-1,2,5,6-dibenzanthracene.
‡ Hexahydro-1,2,5,6-dibenzanthracene.
** Phenanthrene.
*** 40 mice.

1945 ; STEINER and FALK, 1951 ; WARTMAN *et al.*, 1950). As yet, a complete categorization of inhibitors in polluted atmosphere and their effective concentration in relation to the carcinogen present is impossible to prepare ; however one can safely say that inhibitors are present in significant amounts.

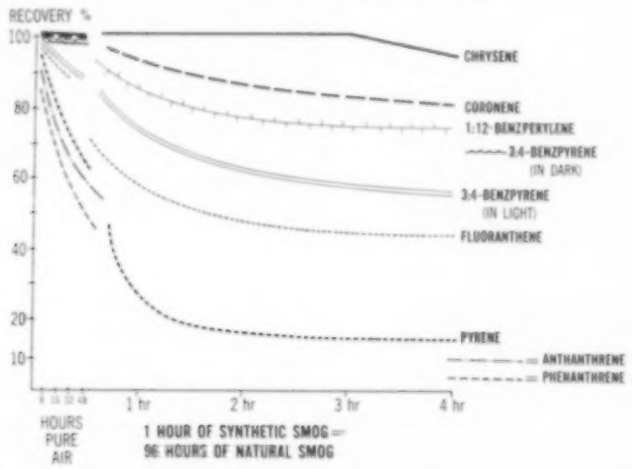

FIG. 3. The disappearance of polycyclic aromatic hydrocarbons on exposure to atmospheric conditions. Stability of 3,4-benzpyrene in polluted air consistent with presence in inspired air of exposed population.

The application of the data just described to the problem of carcinogenic potency of atmospheric pollutants can only be done on a speculative basis at present. What is necessary is a complete roster of carcinogenic aromatic polycyclic hydrocarbons in polluted air. These in all probability will be found adsorbed on soot. This identification represents one of our major undertakings. A second problem with which we

TABLE 4. COMPOUNDS IDENTIFIED OR CHARACTERIZED IN THE PARTICULATE MATTER OF POLLUTED AIR AND TESTED FOR CARCINOGENIC OR ANTICARCINOGENIC PROPERTIES*

Compound or	Partial list of abs. maxima	Carcinogenicity	Anticarcinogenicity
Acenaphthylene		−	
Phenanthrene		−	+
Anthracene		−	+
Pyrene		−	
Fluoranthene		−	
1,2-Benzanthracene		+ +	+
Benz-(*m,n,o*)-fluoranthene		−	
" X "	385, 375, 364, 355, 340	−	
Chrysene		+	+
1,2-Benzpyrene		−	
3,4-Benzpyrene		+ + +	
Anthanthrene		−	
1,12-Benzperylene		−	
11,12-Benzfluoranthene		−	
3,4-Benzfluoranthene		+ +	
Coronene		−	
" Q "	365, 342, 328, 306	not tested	
" R "	426, 400, 382, 365, 353	" "	
" T "	429, 418, 404, 392, 379, 371, 364	" "	
3,4-Benzpyrene quinone		" "	
" U "	414, 392, 372, 346, 330, 316	" "	
Anthanthrone		" "	
" V "	446, 419, 398, 340, 326	" "	
" O "	414, 392, 382, 305, 300, 294	" "	
Phenolic compound	404, 383, 371, 355, 325	" "	

* Inhibitory activity was tested against 1,2,5,6-dibenzanthracene or 9,10-dimethyl-1,2-benzanthracene. None has been tested against 3,4-benzpyrene.
− = No benzpyrene eluted.
+ = Benzpyrene eluted.

are concerned is that of the related compounds which are no longer hydrocarbons but occur rather as phenols and quinones on soot. These too may play a similar role of inhibition over and above any carcinogenic property they may have.

Perhaps the most difficult factor to be accounted for in assessing the carcinogenic potency of the atmosphere resides in the relative instability of the various aromatic polycyclic hydrocarbons adsorbed on soot. Following emission into the atmosphere, some of the smaller 3 ring compounds disappear rapidly. Phenanthrene and anthracene are particularly rapidly lost while pyrene, fluoranthene and anthanthrene disappear to a lesser but still significant degree (Fig. 3). There results thus an ever-changing ratio of potential inhibitor to potential carcinogen as the duration of

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residence time for these compounds in the atmosphere increases. As may be seen, the ratio of pyrene to benzpyrene becomes reverse following average residence in the atmosphere (FALK *et al.*, 1956).

One may conclude from all of this, that for a complete analysis of the carcinogenic hazard of aromatic hydrocarbons found in the atmosphere, a complete testing of the aromatic polycyclic hydrocarbons for both carcinogenic potency and inhibitory effect is necessary. Laboratory analytical studies for bioassay experiments must be performed in parallel. The quantitative aspects of this problem have been worked out in our laboratory through the use of column chromatography with slightly deactivated alumina, ultraviolet absorption spectroscopy, and fluorescence spectroscopy. Specific problems such as the differentiation of 3, 4-benzpyrene and 1, 12-benzperylene and the characterization of compounds eluted together with coronene which possess little characteristic absorption at the concentrations found can be solved through the use of this technique. Identification of compounds has progressed to a point where several additional ones have been recently identified. Good spectra have been obtained for a number of as yet unknown compounds. The list of known carcinogens has not increased dramatically ; however the number of potential modifiers of carcinogenic activity has (Table 4).

A short look into the future strongly indicates that it may be necessary to increase the sensitivity of instruments or to abandon the use of absorption spectroscopy because of the infinitesimal quantities of the compounds being sought out. Fluorescence spectroscopy though useful in quantitation causes destruction of the materials being analyzed because of exposure to the light source ; consequently rapid analysis and a minimum of manipulation are necessary. We have great hopes for the technique of spectrophosphorimetry and hope to be able to report our experience with this analytical instrument in the future.

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SYMPOSIUM ON POLYCYCLIC HYDROCARBONS

FLUORESCENT SPECTRA OF AROMATIC HYDROCARBONS FOUND IN POLLUTED ATMOSPHERE*†

JEROME F. THOMAS, BERNARD D. TEBBENS, ELDON N. SANBORN and JAMES M. CRIPPS
University of California, Berkeley
Sanitary Engineering Research Laboratory
(*Received* 20 *August* 1959)

Abstract—Fluorescent spectrometry offers a very sensitive method of both qualitative and quantitative analysis as, in comparison with other types of spectral analysis, only very small quantities of material are required. The purpose of the paper is threefold: (1) to present a method for obtaining smooth fluorescent curves directly from paper chromatograms; (2) to exemplify the limitations inherent in fluorescent analysis, both qualitative and quantitative; (3) to show smooth fluorescent curves of compounds obtained from polluted atmospheres and compare them with those of compounds of known composition.

INTRODUCTION

A SPECTRAL examination of fluorescent emission offers a very sensitive method of analysis as only minute quantities of material are required compared to all other types of spectral analysis (BOWEN and WOKES, 1953; HAITINGER, 1937; RADLEY and GRONT, 1954). This is very significant in the field of air pollution because over one hundred fluorescent atmospheric contaminants have been isolated in quantities too small for conventional analysis.

These fluorescent atmospheric contaminants have, in most instances, been separated in pure form only on paper chromatograms. A technique was therefore developed which was directly applicable to the samples on paper chromatograms.

In many instances the fluorescence of a compound was found to be enhanced on paper. This is consistent with the theory which states that any factor hindering vibrational modes may favor fluorescence by minimizing the degradation of electronic energy (WEST, 1956). These factors include lowering the temperature, increasing the viscosity of a solvent and adsorption of the fluorescent material on a surface, the latter being the case with paper chromatograms.

Fluorescent analysis has only become practical since recent instrument development has facilitated the attainment of smooth continuous fluorescent curves. The majority of reported fluorescent analytical information has been obtained by means of a spectrograph; information on smooth continuous fluorescent curves is practically nonexistent.

* Presented before the American Chemical Society, Air Pollution Symposium, 136th National Meeting, Atlantic City, N.J., September 1959.

† This work is receiving the support of a research grant RG-4281 of the National Institutes of Health, Public Health Service, and is a co-operative effort within the University of California of the School of Public Health and the College of Engineering.

The purpose of this paper is threefold:

(1) To present a method for obtaining smooth fluorescent curves directly from paper chromatograms;

(2) To exemplify the limitations inherent in qualitative and quantitative aspects of fluorescent analysis;

(3) To present smooth fluorescent curves of hydrocarbons obtained from polluted atmospheres compared to hydrocarbons of known composition.

It should be mentioned that the hydrocarbons discussed represent less than 25 per cent of the total number of fluorescent compounds isolated from typical polluted atmospheres.

INSTRUMENTATION

Fluorescent analysis of the type herein described requires a monochromator of good resolution; a photomultiplier detector; and a linear energy feedback coupled to a

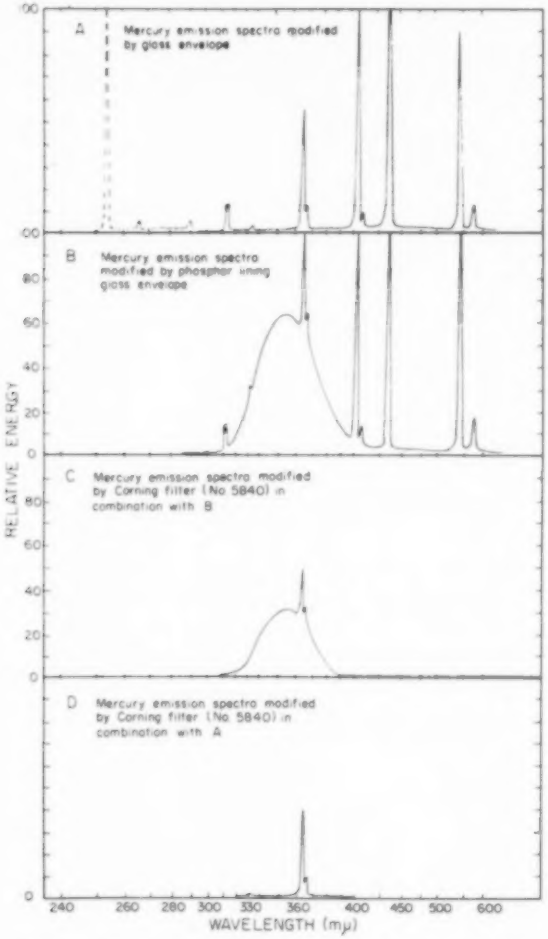

FIG. 1. Graphical evaluation of ultraviolet energy source.

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recorder with a wave-length drive. This system plots the wave length, generally measured in millimicrons (mμ), against the fluorescent energy. The fluorescent energy is dimensionless as it is measured relative to the background energy reaching the detector. The background energy was found to be negligible for all slit widths in the operating range. These various instrumental components are incorporated directly into a Beckman Model DK-2 spectrophotometer on which all reported spectral measurements were made.

The ultraviolet irradiation source is also of extreme importance. For normal

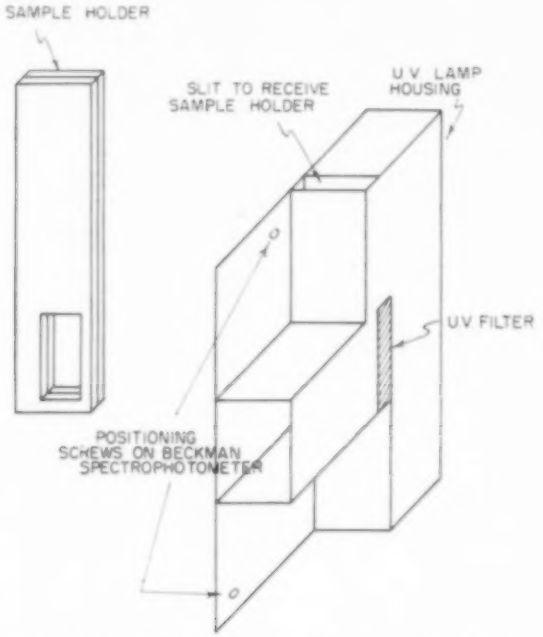

FIG. 2. Schematic drawing of sample holder and mercury lamp housing (designed to fit Beckman Model DK-2 spectrophotometer).

operation, i.e., recording of curves above 400 mμ, a tubulated mercury lamp (G.E. F4T5/BL) was found to be most efficient because it allowed direct irradiation over the entire paper strip without the inherent energy loss of an optical system required by a point source of light. The phosphor coating on the inside of the lamp broadens the mercury bands in the region between 300–390 mμ, thus encompassing the major portion of the u.v. absorption curves of the compounds under investigation, which is a requisite for fluorescence. To obtain fluorescent curves in the region between 375–400 mμ, as is occasionally required, a mercury lamp devoid of the phosphor is used. It is impossible to go below 375 mμ because of the overlap of fluorescence and absorption bands. In general, operation below 400 mμ should be avoided because of possible errors in interpretation which may be introduced due to such an overlap and to the interfering presence of mercury bands.

In combination with the ultraviolet energy source is a Corning filter (No. 5840) interposed between the mercury lamp and the sample, which allows the ultraviolet

irradiation of the sample yet eliminates any visible light originating at the u.v. source from reaching the detector. Aqueous solutions of nickel, cobalt and copper salts in quartz cells were found to have occasional special application as filters (BOWEN and WOKES, 1953). Fig. 1A shows an emission curve for a mercury lamp devoid of the phosphor lining; the bands below 290 mμ are missing because of the low cut-off limit of the glass envelope. An emission curve for an identical lamp with phosphor lining is shown in Fig. 1B; the increased energy output in the 365 mμ region is very evident. The effect of introducing filters is demonstrated in Figs. 1C and 1D:

(1) There is an overall loss in energy;
(2) All bands above 390 mμ have been eliminated with the background energy in the visible region being negligible;
(3) The superior efficiency of the proposed system is clearly indicated.

A schematic drawing of the mercury lamp housing and sample holder is shown in Fig. 2. As indicated in the figure, the irradiating source, sample and monochromator entrance aperture are in alignment as found necessary for maximum resolution of the fluorescent spectra. Approximately 10 per cent greater efficiency is obtained if light scattering through the paper is minimized by subjecting the chromatogram spot to considerable pressure (20,000 lb/in²).

In normal operation the spectrophotometer entrance slit is opened only wide enough to allow maximum resolution of the principal fluorescent band. The scanning speed should be very rapid (median rate: 100 mμ per 90 sec), limited only by the pen response rate, as many fluorescent compounds are light-sensitive. This latter phenomenon will be discussed subsequently in greater detail.

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The magnitude of background noise is indicated in Figs. 6 and 7, which show several typical fluorescent curves as recorded directly on the spectrophotometer. It should be noted that all other fluorescent curves shown have had the background noise removed as a drafting expediency.

RESULTS AND DISCUSSION

Qualitative aspects

The paper chromatograms used for fluorescent measurements were prepared using techniques previously reported (THOMAS *et al.*, 1957) in addition to newly reported techniques involving acetylated paper (SPOTSWOOD, 1959). Several significant chromatographic developments, which will be presented in a later publication, were used to obtain complete resolution. The amount of material required in a chromatogram spot for fluorescent analysis is of the order of 1 μg contained in a circle approximately 2 cm in diameter. Sample size will be covered in greater detail under quantitative aspects.

All qualitative aspects are discussed on the basis of data contained in three figures, the curves being referred to by keyed letters. Smooth continuous fluorescent curves of hydrocarbons obtained from polluted atmospheres matched with hydrocarbons of known composition are shown in Fig. 3. Fluorescent curves of additional hydrocarbons of known composition, whose presence has not been detected in polluted atmospheres by the fluorescent technique, are shown in Fig. 4. Fluorescent curves of hydrocarbons of unknown composition separated from polluted atmospheres are shown in Fig. 5. Also shown in these figures are the exact wave-length positions of each set of bands which are characteristic of individual compounds.

The curve for 1,2-benzanthracene (A) is very characteristic and significant, showing four bands of decreasing intensity with increasing wave length. Previously reported spectrographic work (HEIGER, 1930) has referred to the three major bands as " Schroeter bands " and assigned wave lengths of 4000, 4180 and 4400 Å. A hypsochromic shift is exhibited in the smooth fluorescent curve with the major bands at 385, 410 and 434

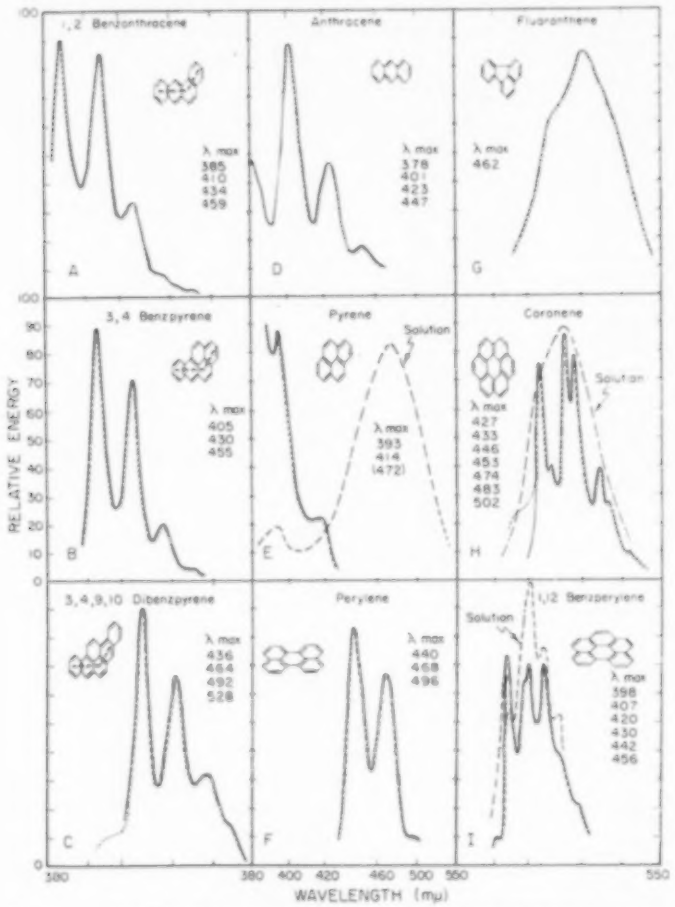

FIG. 3. —— Matching fluorescent curves of hydrocarbons of known composition.
- - - - - Curves of hydrocarbons obtained from polluted atmospheres.

mμ, but it should be noted that the increments between these bands are identical with those reported in the spectrographic data above. In addition to the three major bands it is possible to observe a fourth small band in the smooth fluorescent curve at a wave length of 459 mμ.

This grouping of the three major bands was found to be characteristic of all hydrocarbons that incorporate the basic structure of 1,2-benzanthracene; a basic structural comparison for 3,4-benzpyrene (B) and 3,4,9,10-dibenzpyrene (C) is exemplified in Fig. 3 by means of dotted lines in the structural formulas. If the hydrocarbon does not contain this basic structure it is not possible to predict the shape of the curve.

The basic structure of 1,2-benzanthracene was also found by FIESER (1954) to be one of the requisites for carcinogenic activity in condensed polynuclear aromatic-type hydrocarbons. All carcinogenic hydrocarbons analyzed by the proposed technique incorporate this basic structure and exhibit the characteristic curve as exemplified in curves B, C, L, M and N. Thus a knowledge of fluorescent spectroscopy might be

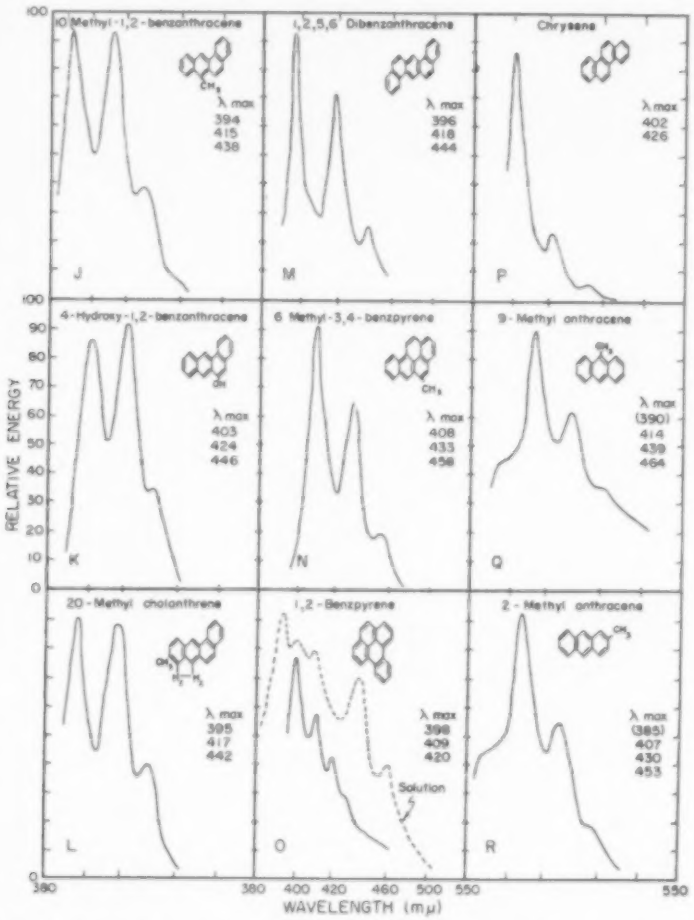

FIG. 4. Fluorescent curves of hydrocarbons of known composition whose presence has not been detected in polluted atmospheres.

useful in predicting the presence of a polynuclear aromatic hydrocarbon having carcinogenic activity even without knowing its identity. For example, in Fig. 5, curves X-1, X-5 and X-6 are not indicative of carcinogenic activity; curves X-2 and X-8 appear to be likely suspects.

A comparison of fluorescent curves obtained from paper chromatograms to the curves obtained from solution, shows a similarity for all compounds tested if the compound under investigation incorporates the basic structure of 1,2-benzanthracene. This is exemplified for curves B, C, J, L, M and N. The curve for 4-hydroxy-1,2-

benzanthracene (K) is an apparent exception because the middle band is slightly larger, but the compound itself is not a pure hydrocarbon. If the compound under investigation does not incorporate the basic structure of 1,2-benzanthracene there is no

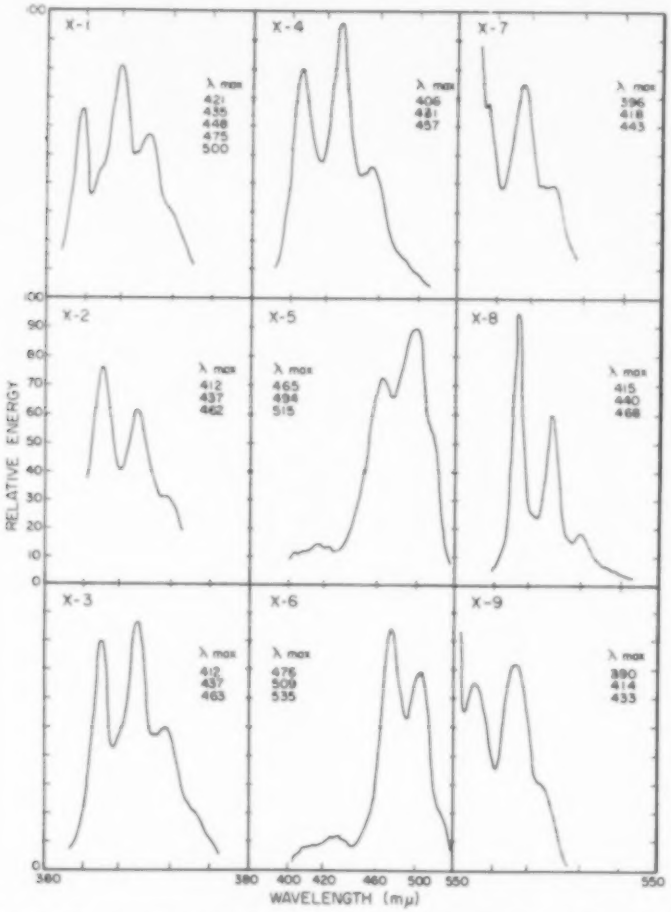

FIG. 5. Fluorescent curves of hydrocarbons of unknown composition whose presence has been detected in polluted atmospheres.

apparent similarity in many cases. Fluorescent solution curves for pyrene (E), coronene (H), 1,12-benzperylene (I) and 1,2-benzpyrene (O) exhibit this dissimilarity.

The effect of adding a methyl group to the aromatic nucleus is indicated by comparing curves A and J; B and N; and D, Q and R. In every case there is a bathochromic shift that can be definitely measured. In contrast to ultraviolet absorption curves, fluorescent spectroscopy shows a positive differentiation between parent hydrocarbon and methyl substituted derivatives.

Although the position of the principal bands of several compounds apparently match, this anomaly can be resolved immediately by comparing Rb values for the compounds in question. For example, curves X-2 and X-3 have Rb values of 2·9

and 1·3 respectively (using 3,4-benzpyrene as the control); curves M and X-7 have Rb values of 2·7 and 2·0 respectively; curves B and N have Rb values of 1·0 and 1·6 respectively. Thus a combination of chromatography and fluorescent analysis offers an excellent means for positive identification of these hydrocarbons.

It is interesting to note that the presence of 1,2,5,6-dibenzanthracene (M) in polluted atmospheres has been reported by ourselves as well as other investigators (RADLEY and GRONT, 1954). On the basis of fluorescent analysis its presence is not indicated. There are other condensed polynuclear aromatic hydrocarbons reported

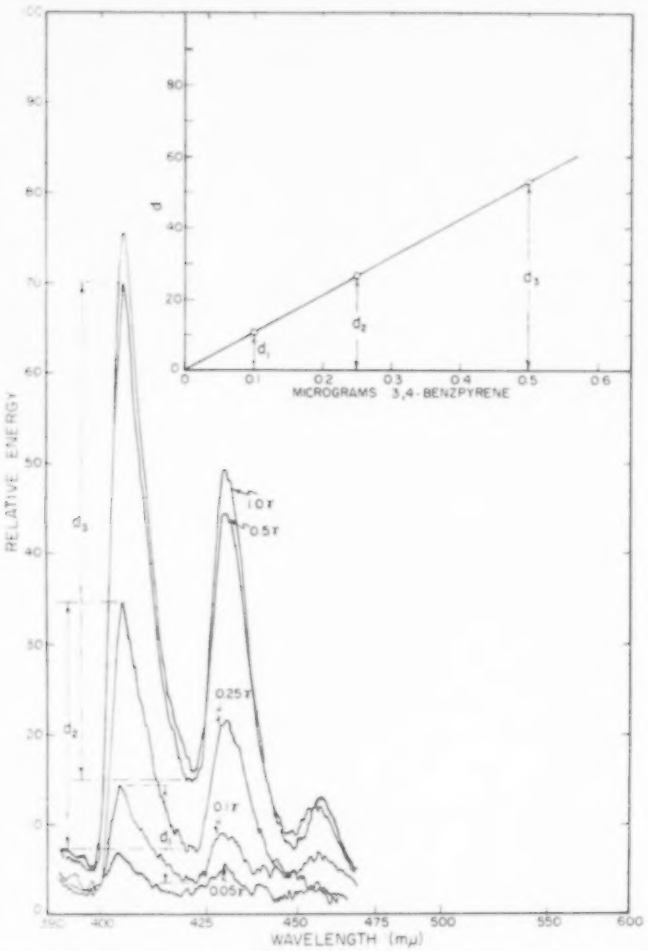

FIG. 6. Standard curve for the quantitative analysis of 3,4-benzpyrene (Insert) based on fluorescent curves.

present in polluted atmospheres whose presence cannot be detected by the proposed technique because they do not fluoresce; for example, naphthacene and pentacene.

Quantitative aspects

A series of curves exemplifying the quantitative technique is shown in Fig. 6. A

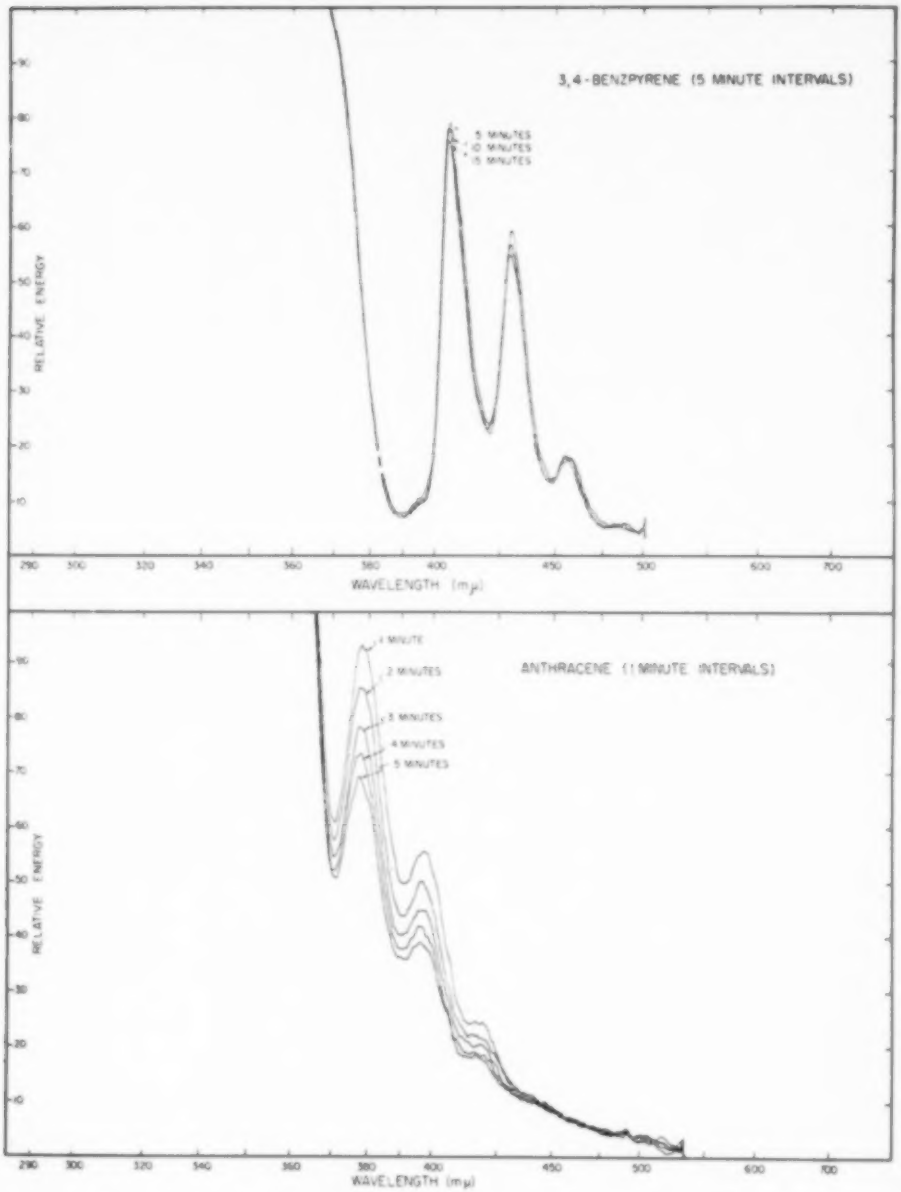

FIG. 7. Effect of ultraviolet radiations on fluorescent curves with respect to time.

standard curve for 3,4-benzpyrene was prepared by maintaining a uniform spectrophotometer program, varying only the amount of 3,4-benzpyrene contained in the chromatogram spots. The distance measured from the peak of the principal band to the adjacent longer wave-length pit was used as a measure of concentration as indicated in the figure. The measured distance plotted against concentration gives a straight line

between 0·01 and 0·5 μg of 3,4-benzpyrene. Above 0·5 μg the curve rapidly falls off to a plateau; for qualitative work, values up to several micrograms may be used. The lower *practical* limit is set at 0·1 μg for several reasons:

(a) Below this limit the distance from peak to pit is very small introducing possible errors in measurement. Reprograming the spectrophotometer for the smaller values exceeds the recorder range for the upper values thus requiring a second standard curve for the very low range;

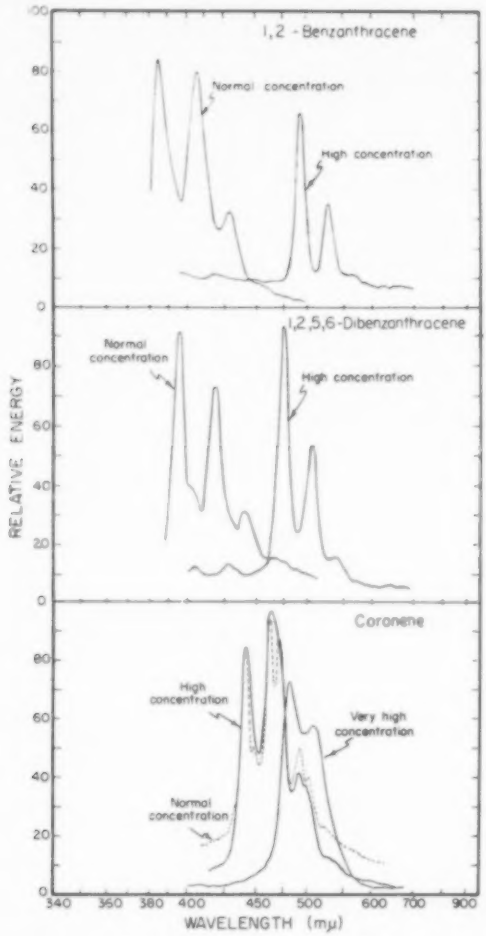

FIG. 8. Apparent concentration effect on fluorescent curves (self-quenching or autoabsorption).

(b) A more important reason is that below 0·1 μg it is very difficult visually to detect 3,4-benzpyrene on the paper so that the position of the spot to be removed for fluorescent analysis cannot be determined accurately.

Comparable quantitative results were obtained using other hydrocarbons.

There are several difficulties in quantitative analysis which may be overcome by using freshly prepared chromatograms and also by operating below a critical concentra-

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tion (the suggested operating range falls below this critical value). These two difficulties will be discussed in more detail.

Many fluorescent compounds are light-sensitive to various degrees; there is an apparent decrease in concentration as the compounds are exposed to light. For example, the fluorescent curves for anthracene and 3,4-benzpyrene were run between the limits of 390 and 600 mμ, as shown in Fig. 7, allowing definite time intervals between runs but not varying the spectrophotometer program. The concentration apparently decreases for both compounds with time but more rapidly for anthracene. This apparent decrease is probably due to a reversible oxygenation of the hydrocarbon to photoxides and resembles the reversible oxygenation of hemoglobin to oxyhemoglobin (FIESER *et al.*, 1944); the oxygen addition destroys the resonating system necessary for fluorescence. As mentioned, the situation can be remedied by using freshly prepared chromatograms.

The amount of material contained on the paper strips is very important because of the phenomenon of self-quenching or autoabsorption. Each compound has a critical value above which self-quenching occurs. These values were not determined in this work because ordinary paper chromatographic techniques necessitate working in quantities that fall below the critical value. Self-quenching becomes apparent in either of two ways:

(1) Fluorescent bands in the shorter wave-length region become small or disappear while a new set of bands appear at longer wave lengths;
(2) The characteristic fluorescent curve suffers a broadening of the principal bands accompanied by considerable loss in fine structure.

These phenomena are exemplified in Fig. 8, which shows the appearance of new bands at long wave lengths for 1,2-benzanthracene and 1,2,5,6,-dibenzanthracene, while the latter characteristic noted may be observed for coronene. It is felt that only smooth fluorescent curves obtained at concentrations below the critical level are significant from both a qualitative and a quantitative point of view.

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SYMPOSIUM ON POLYCYCLIC HYDROCARBONS

POLYNUCLEAR AROMATIC HYDROCARBONS IN THE PARTICULATES OF DIESEL EXHAUSTS IN RAILWAY TUNNELS AND IN THE PARTICULATES OF AN URBAN ATMOSPHERE*

GEORGE EVAN MOORE† and MORRIS KATZ‡

(*Received* 6 *August* 1959)

Abstract—This paper describes work on the identification of polynuclear aromatic hydrocarbons in the particulate matter arising from the operation of heavy diesel locomotives in railway tunnels, and includes a comparison of results with those derived from a similar analysis of particulates collected from an urban atmosphere.

The results indicate that, although the operation of diesels in the tunnels increased the particulate loading of the tunnel atmospheres to some eight times the loading of the general urban atmosphere, the detectable amounts of polynuclear aromatic hydrocarbons were such as might be found in the particulates carried into the tunnel by ventilating air. No hydrocarbons were found in the tunnel particulates which were not found in the particulates collected at the top of a ten story building adjacent to one of the tunnels, and it is concluded that the production of polynuclear aromatic hydrocarbons in the cylinders of efficiently operated diesel locomotives is negligible in comparison with the formation of this group of hydrocarbons by general combustion of fuels in urban activities.

The methods used were chromatographic and spectrophotometric, and included fractionation of benzene extractable organic fractions into aliphatic, aromatic and oxygenated groups on silica gel columns, the further chromatography of aromatic groups on alumina, identification of hydrocarbon species by comparison of analytical spectrograms with published ultraviolet spectra and spectra of reference samples, and quantitative estimation of concentrations by the base line technique.

Polynuclear aromatic hydrocarbons identified in urban air samples were fluorene, anthracene, pyrene, fluoranthene, 1,2-benzanthracene, 1,2-benzpyrene, 3,4-benzpyrene, 1,2-benzperylene and coronene. Spectrograms for tunnel samples showed in some cases small peaks which were characteristic of some of these hydrocarbons, and in other cases only suggestive shoulders or inflections.

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INTRODUCTION

DIESEL engines as contributors to the contamination of urban atmospheres are minor factors in comparison with industrial and domestic fuel-burning equipment, automobiles, industrial processes and incinerators. In circumstances where diesel emissions are not dissipated rapidly, however, the gaseous and solid constituents are potential health hazards which require appraisal.

This paper reports the results of an examination of particulate matter collected from the air of railway tunnels during the operation of 1750 h.p. diesel locomotives, and a comparison of results with those of the examination of reference samples of particu-

* Presented before the American Chemical Society, Air Pollution Symposium, 136th National Meeting, Atlantic City, N.J., September 1959.

† Occupational Health Division, Department of National Heath and Welfare, Ottawa, Canada.

‡ Consultant, Occupational Health Division, Department of National Health and Welfare, Ottawa, Canada.

lates collected from urban air. The work was made possible by the participation of the Department of National Health and Welfare in two comprehensive investigations of railway tunnel atmospheres, in co-operation with the Research and Development Department of the Canadian National Railways. A detailed report of the gaseous and particulate concentrations found in one of the investigations and an appraisal of the potential health hazards with respect to gases has been presented elsewhere (KATZ *et al.*, 1959).

Gaseous emissions of diesel motors operating in mines have been discussed in U.S. Bureau of Mines Publications (HOLTZ *et al.*, 1940–3) and variations of output of carbon monoxide, aldehydes, and oxides of nitrogen by diesels and automobiles in relation to operating variables have also been studied (FAITH, 1954; FITTON, 1954). The associated problem of assessing the significance of the solid constituents of exhaust emissions, with special regard to the carcinogenic hydrocarbons extractable from the solids has been dealt with by KOTIN *et al.* and by COMMINS *et al.* KOTIN has reported that an inefficiently operated diesel can be an incomparably greater source of aromatic hydrocarbons than an automobile, but that a diesel in excellent working condition emits only traces. COMMINS measured concentrations of polynuclear aromatic hydrocarbons in the atmospheres of diesel bus garages in London and found that, while the smoke concentrations in the naturally ventilated garages during periods of bus activity reached values which were some three or four times the concurrent values in outside air, equal volumes of inside and outside air contained about the same amounts of hydrocarbons. It was concluded that the smoke or particulate matter produced by diesel bus motors contained a much lower proportion of aromatic hydrocarbons than smoke produced by general urban activity.

The tunnel studies, described in greater detail in the paper referred to above (KATZ *et al.*, 1959), were initiated to appraise the practicability of operating diesel locomotives directly through the tunnels in the course of routine traffic movement as an alternative to the customary time-consuming and expensive change to electric haulers for tunnel traffic. One detail of the sampling programs was the collection of high volume filter samples of particulates to determine dust loadings, and it was recognized that analysis of the samples for polynuclear hydrocarbons would indicate the degree to which these products of combustion were produced in the large cylinders of diesel locomotives. Some estimate of the occupational health hazard to personnel, whose duties included prolonged exposure to tunnel atmospheres, could thus be made, that is in so far as the health hazard was related to the inhalation of potentially carcinogenic hydrocarbons.

A comparison is useful of some of the conditions dealt with in the tunnel studies and in the studies by COMMINS *et al.* (1957) of the atmospheres of diesel bus garages The first considered the effects of a relatively small number of high horsepower locomotives, the latter the effects of a large number of smaller engines. Natural ventilation was much less effective in the tunnels than in the garages in diluting exhaust emissions. Only warmed-up engines, usually in motion, contributed combustion products to tunnel atmospheres; diesel motors which were starting, warming up and idling contributed their varying amounts of gases and particulates to the air of the garages. Grossly inefficient operation of diesel motors was a factor in neither tunnel nor garage investigations. COMMINS *et al.* (1957) note that London Transport Authority customarily derate their engines by 10 per cent to minimize heavy smoke emission.

MATERIALS AND INSTRUMENTS

Iso-octane (2,2,4-trimethylpentane) Certified, Enjay Company, Inc.
*Cyclo*hexane, practical, Eastman Kodak Company.
Benzene, reagent grade, Baker and Adamson.
Alcohol, absolute.

Iso-octane and *cyclo*hexane were purified by passing through $2\frac{1}{4} \times 12$ in. columns of activated silica gel (Davison 28/200). *Cyclo*hexane required the passage through two columns in succession to remove traces of benzene structure in spectrograms of samples.

Benzene was used without purification. Spectrograms of the residues of evaporated benzene samples dissolved in *cyclo*hexane showed small absorptions at short wavelengths in a range which did not interfere seriously with absorption readings for polynuclear aromatics.

Activated alumina—Type " H ", 100–200 mesh, Peter Spence and Sons, Ltd., Widnes, Lancs. Activity was adjusted by drying overnight at 115°C and adding 4 per cent water to the oven dry weight.

Activated silica gel—Davison, 28–200 mesh, commercial desiccant.

Spectrophotometer, Perkin–Elmer Spectracord, Model 4000, ultraviolet recording.

ANALYTICAL SAMPLES

The scheduled operation of high volume filters in the St. Clair Tunnel, Sarnia, Ontario and in the Mount Royal Tunnel, Montreal, Que., described elsewhere (KATZ *et al.*, 1959) afforded oven-dry samples of particulate matter deposited on flash-fired fiber glass filters. For the Mount Royal Tunnel sampling schedule a high volume sampler was operated concurrently outside the tunnel on the roof of an adjacent ten-story building. This furnished reference samples representative of the prevailing urban particulate pollution. From the ratios of particulate loadings of the atmospheres inside the tunnel and outside, which were of the order of eight or ten to one, it may be deduced that the bulk of the particulates collected in the tunnels arose from the operation of the locomotives.

Measurements were also made on an hourly basis by A.I.S.I. Automatic Smoke Samplers and the particulate concentrations inside and outside the tunnels were recorded by evaluation of the optical density of the spots of particulate matter on filter tape in terms of Coh units per 1000 linear feet of air. It was found in the Mount Royal Tunnel, for example, that, during inactive periods, the smoke concentrations ranged from about 1 to 5 Coh/1000 ft, or only about 1 Coh unit higher than the range measured at the outside, urban air stations. On the other hand during periods of active diesel train movement the smoke concentrations ranged from 7 to 47 Coh/1000 ft, depending upon the location of tunnel sampling stations.

ANALYTICAL PROCEDURE

Oven drying of particulates from which a benzene soluble organic fraction is to be extracted is, of course, undesirable. COMMINS and LAWTHER (1958) have shown that the volatility of 3,4-benzpyrene is appreciable at 100°C. In the tunnel investigations, oven drying was kept to the minimum consistent with reliable weight determinations, and the finding of appreciable quantities of a wide variety of aromatics in the control

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sample leads to the conclusion that no substantial loss of aromatics occurred on oven drying the samples.

The organic fraction of particulate matter is here defined as that fraction extractable in a Soxhlet with benzene. The reference sample, representative of general urban pollution in Montreal, consisted of 480 mg of material collected on seven fiber glass filters. The filters were cut to a size convenient to the dimensions of the extraction sections of two Soxhlets, wrapped loosely in bundles and placed in the Soxhlets without thimbles. About 400 ml of benzene were used in each and extraction was carried out for 8 hr. The bulk of the solvent was evaporated from the two lots of benzene extract, they were then combined, filtered and taken to dryness in a current of dry air. The reference sample of particulates yielded 66 mg of benzene extractable.

A tunnel sample of 740 mg of particulates on four filters was extracted similarly in one Soxhlet and yielded 77 mg of benzene extractable.

Silica gel columns were used in the established manner (TABOR *et al.*, 1956) to divide both portions of benzene extractable organics into aliphatic, aromatic and oxygenated fractions. The results are summarized in Table 1.

The aromatic fractions of the respective silica gel separations were taken up on small weights of deactivated alumina and added to the tops of packed alumina columns about 1·5 × 10 cm and containing about 18 g of deactivated alumina. The chromatographic techniques used were essentially those described by COOPER (1954), WEDGWOOD and COOPER (1953) and COMMINS (1958). Elution fractions of varying size were collected, usually directly in the 1 cm cells of the spectrophotometer, and spectrograms were run immediately the fractions were collected. Where judgment indicated, fractions were combined and rechromatographed. Materials not removable from the columns by elution with *cyclo*hexane were eluted by mixtures of *cyclo*hexane and benzene and pure benzene. The solvents were evaporated by a stream of dry air, the residues were dissolved in *cyclo*hexane and spectrograms were run at suitable concentrations.

TABLE 1. CHROMATOGRAPHIC SEPARATION ON SILICA GEL OF BENZENE EXTRACTABLE ORGANICS INTO ALIPHATIC, AROMATIC AND OXYGENATED FRACTIONS

	Reference sample		Tunnel sample	
	(mg)	(%)	(mg)	(%)
Weight of particulate sample	478		741	
Weight of benzene extractable	65·9	100	77·0	100
Iso-octane elution (aliphatic)	8·4	12·7	29·3	38·0
Benzene ,, (aromatic)	41·0	62·2	26·1	33·9
Alcohol ,, (oxygenated)	14·3	21·7	17·5	22·7
Total recovered	63·7	96·6	72·9	94·6

For the identification of some of the individual aromatic hydrocarbons reliance was placed mainly on a comparison of the spectra with those published in the literature (FRIEDEL and ORCHIN, 1951). The shortcomings of this method will be discussed

later. For the identification and quantitative estimation of a few hydrocarbons by the base line method (COOPER, 1954), reference spectra of the hydrocarbons in *cyclo*-hexane were prepared.

RESULTS

Background absorption

The spectra of chromatographic fractions of tunnel material, and, to a lesser degree, material collected from urban air, were characterized by heavy structureless background absorption. Comparison of the analytical spectrograms with published spectra or with prepared spectrograms of reference samples of pure hydrocarbons was consequently difficult and uncertain. The results of an attempt to assess the effects of background material are shown in Figs. 1, 2 and 3. The lower curves of each figure

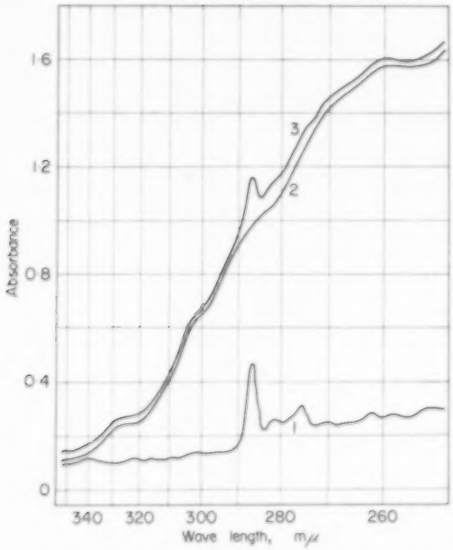

FIG. 1. Ultraviolet spectrograms showing: (1) fluoranthene in *cyclo*hexane at 1 μg/ml concentration, (2) a typical spectrogram for tunnel material, (3) spectrogram resulting from addition of 1 μg/ml of fluoranthene to 2.

are spectrograms of solutions in *cyclo*hexane of fluoranthene, 1,2-benzanthracene and chrysene; the middle curves are spectrograms for 3 ml samples of a chromatographic fraction of tunnel particulates; the upper curves were produced by adding 10μl of solutions of the three hydrocarbons to the 3 ml samples of the chromatographic fraction. The concentration of the unknown which produced the heavy background absorption was thus decreased only slightly, and differences in absorption between the upper and middle curves indicate the fidelity with which characteristic peaks for the three hydrocarbons are recorded in the presence of the heavily absorbing unknown material. The heights of the superimposed peaks were found to be roughly proportional to the calculated increments in concentration for each of the three hydrocarbons.

It was concluded from these results that the small dimensions of characteristic peaks in the spectra of tunnel particulate fractions indicated the presence in the samples of

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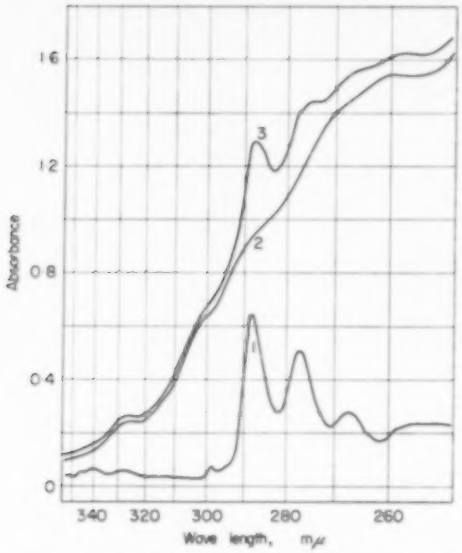

FIG. 2. Ultraviolet spectrograms showing: (1) 1,2-benzanthracene in *cyclo*hexane at 1·4 μg/ml concentration, (2) a typical spectrogram for tunnel material, (3) spectrogram resulting from addition of 1 μg/ml of 1,2-benzanthracene.

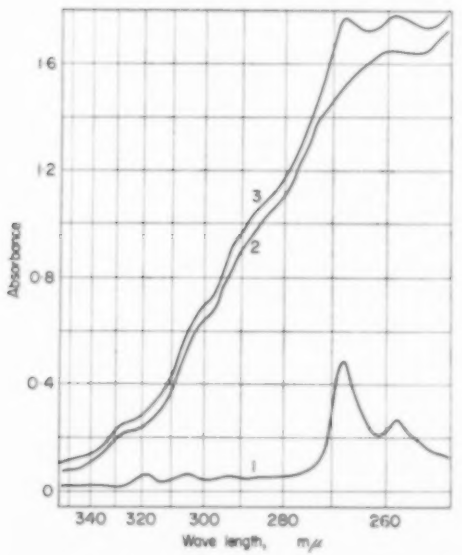

FIG. 3. Ultraviolet spectrograms showing: (1) chrysene in *cyclo*hexane at 0·84 μg/ml concentration, (2) a typical spectrogram for tunnel material, (3) spectrogram resulting from addition of 0·5 μg/ml of chrysene to 2.

no more than traces of the various hydrocarbons which were found with relative ease in samples of particulates collected outside the tunnel. Obviously, the ultraviolet spectrometry yielded little information with respect to the identity of the heavily absorbing background material. Three infrared spectrograms, Figs. 4, 5 and 6, show marked similarity to a spectrogram for a carbon tetrachloride extract of particulates

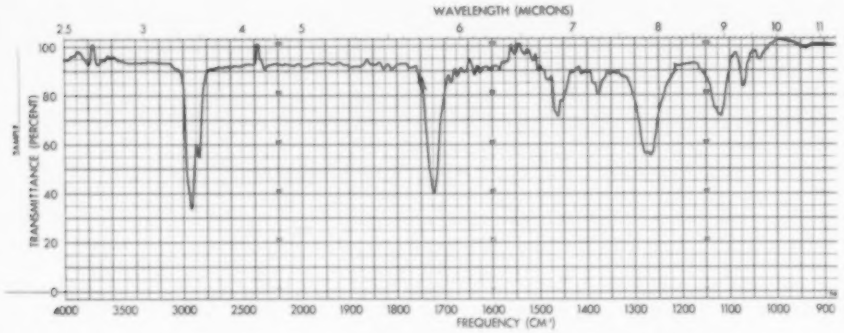

FIG. 4. Infrared spectrogram of an elution fraction of Montreal particulates.

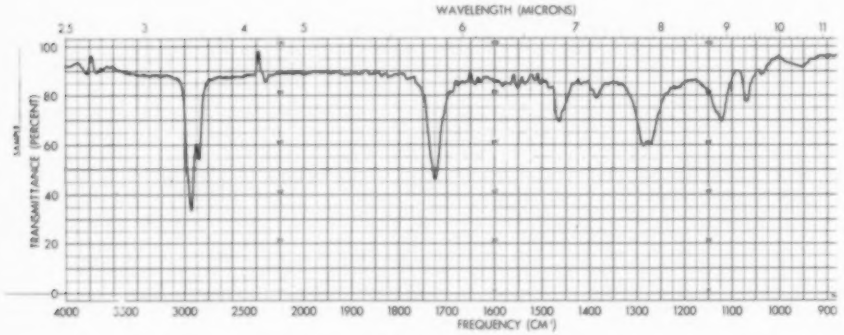

FIG. 5. Infrared spectrogram of a later elution fraction of Montreal particulates.

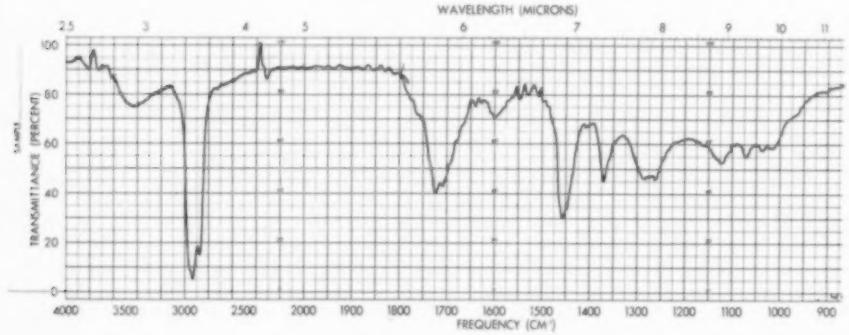

FIG. 6. Infrared spectrogram of an elution fraction following coronene, St. Clair Tunnel particulates.

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collected in Windsor, Ontario as described by SHORE and KATZ (1956). The similarity of infrared spectra for a sample of the whole extract of Windsor particulates and for different elution fractions of the extract of Montreal particulates and St. Clair tunnel particulates suggests that infrared absorption peaks are probably attributable to hydrocarbon constituents common to all, most likely the material which is responsible for the background of interfering, heavy ultraviolet absorption.

The background absorption, so pronounced in spectrograms of tunnel material, was less evident when dealing with particulates collected from outside the tunnel. It was far from absent, however, and the trouble encountered in the chromatographic resolution of mixtures of aromatic hydrocarbons prompts the surmise that much uncertainty would be avoided if the background material were identified and means devised of separating it.

Tunnel particulates

Two spectrograms for tunnel hydrocarbons are shown in Figs. 7 and 8. They are exceptional in that the peaks are more sharply defined than in the large majority of spectral curves for tunnel material.

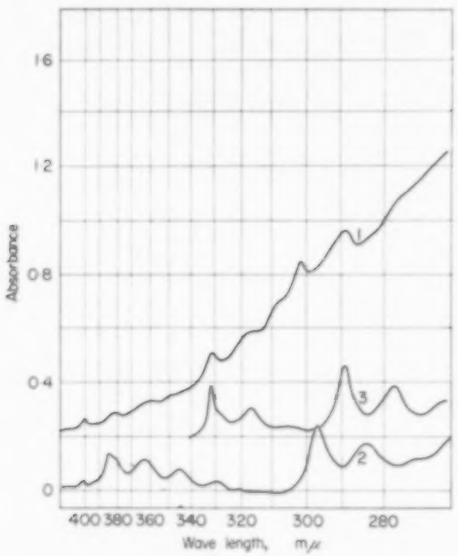

FIG. 7. Ultraviolet spectrogram for a chromatographic fraction of tunnel material showing: (1) trace indications of 1,2-benzpyrene and 3,4-benzpyrene, (2) reference curve for 3,4-benzpyrene, (3) reference curve for 1,2-benzpyrene.

Curves 2 and 3 in Fig. 7 are spectrograms for reference solutions of 3,4-benzpyrene and 1,2-benzpyrene. The analytical spectrogram, curve 1, is for a chromatographic fraction of 20 ml of *cyclo*hexane elutant reduced in volume by evaporation to 5·6 ml. Coincidence of peaks on the analytical curve and on the 1,2-benzpyrene curve at 288 mμ and 331 mμ establishes the presence in the sample of 1,2-benzpyrene. A peak at 302 mμ may indicate 1,12-benzperylene and a small one at 402 may be indicative of 3,4-benzpyrene. These identifications are consistent with the circumstances that a point in the elution had been reached where a relatively large volume of pure *cyclo*-

hexane was required to remove detectable quantities of material from the column. In subsequent elution of more strongly absorbed members of the hydrocarbon series a 90–10 mixture of *cyclo*hexane and benzene was used.

The effect of increasing the polarity of the eluting solvent is shown in Fig. 8. The fraction whose spectrogram is shown consisted of 7·2 ml of the mixed elutant which

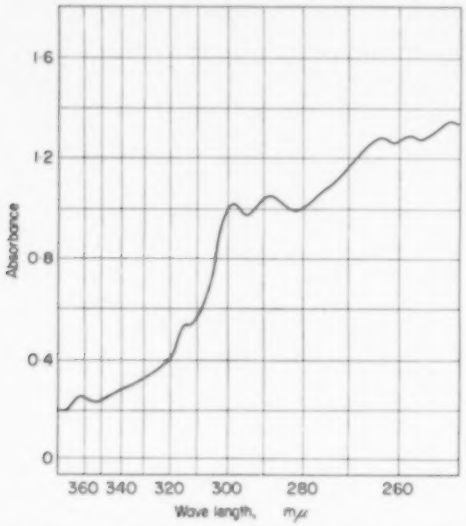

FIG. 8. Ultraviolet spectrogram for a chromatographic fraction of tunnel material showing continued presence of 1,2-benzpyrene and 3,4-benzpyrene and a new peak indicative of 1,12-benzperylene.

was evaporated and made up to 3·9 ml with pure *cyclo*hexane. The volume of elutant which intervened between the fractions of Figs. 7 and 8 was 12 ml. The emergence of a small broad peak at about 363 mμ, not evident in Fig. 7, probably indicates increasing concentration of 1,12-benzperylene. Peaks at 315 mμ, 298 mμ, 288 mμ, characteristic of 3,4-benzpyrene and 1,2-benzpyrene persist in Fig. 7 with relative proportions somewhat changed.

In addition to the compounds identified by the obviously tenuous evidence available from Figs. 7 and 8, pyrene and coronene were identified with greater certainty, others such as 1,2-benzanthracene and chrysene with less.

Further detailed description of trace indications, such as small shoulders and slight inflections in the spectral curves, of other polynuclear hydrocarbons would be tedious and would add nothing to the conclusion that the hydrocarbons identifiable in the extract of particulates collected outside the tunnel were present in the tunnel particulates in no more than trace amounts.

Urban particulates

The aromatic fraction of the benzene extract of particulates collected from city air outside the tunnel totalled 41 mg, as shown in Table 1. This total is in reality the sum of two elution fractions, the first 100 ml of benzene yielding on evaporation 13·7 mg of residue, the second 300 ml of benzene yielding 27·3 mg. The reason for dividing the aromatic fraction into two parts was that the initial 100 ml elution was noticeably

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colored as it left the silica gel column; the following 300 ml were colorless. All the polynuclear aromatic hydrocarbons whose identity was established by subsequent chromatography on alumina and spectroscopy were found in the initial 13·7 mg fraction of the aromatics. The remaining 27·3 mg exhibited after similar examination, only the heavy featureless ultraviolet absorption referred to previously.

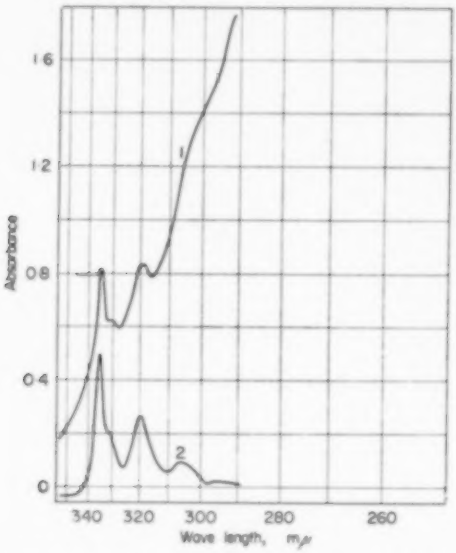

FIG. 9. Ultraviolet spectrograms showing: (1) pyrene in an urban air chromatographic fraction, (2) reference spectrum for pyrene in *cyclo*hexane at 1·7 μg/ml concentration.

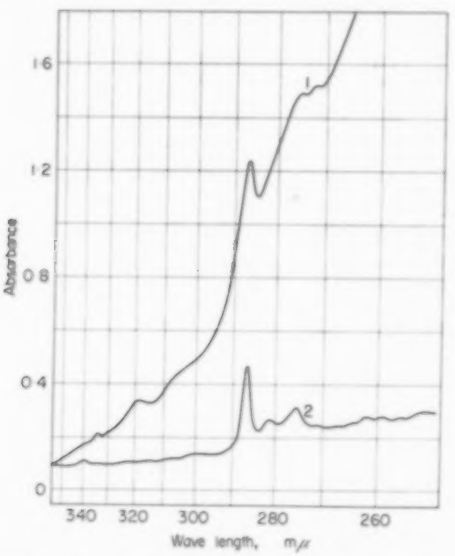

FIG. 10. Ultraviolet spectrograms showing: (1) fluoranthene in an urban air chromatographic fraction, (2) reference spectrum for fluoranthene at 1·8 μg/ml concentration.

These observations are described in some detail because they may indicate a promising approach to the problem of eliminating the heavily absorbent background material from chromatographic fractions intended for spectroscopic examination, detailed paper chromatography or gas chromatography.

The primary purpose of the analysis of particulates collected outside the tunnel was to assess the reliability of methods which revealed no more than trace amounts of

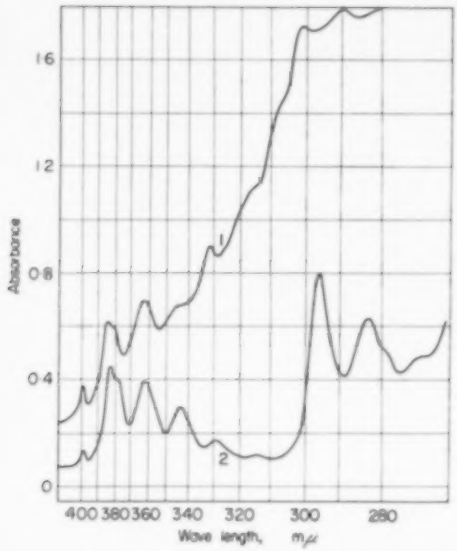

FIG. 11. Ultraviolet spectrograms showing: (1) 3,4-benzpyrene in an urban air chromatographic fraction, (2) reference spectrum for 3,4-benzpyrene in *cyclo*hexane at 4·6 μg/ml concentration.

hydrocarbons in tunnel particulates. If the aim had been to determine the aromatic hydrocarbon content of urban air, a more detailed sampling schedule would have been organized, and oven drying of the particulates would have been avoided. The results were gratifying in that the methods used for tunnel material when applied to outside air particulates detected the polynuclear aromatics which are of special interest, some of them in amounts permitting quantitative estimation.

Analytical curves for pyrene, fluoranthene, 3,4-benzpyrene and coronene are shown in Figs. 9, 10, 11 and 12. Each figure shows also a reference spectrum for a known concentration of the hydrocarbon. Curves from which the presence was deduced of fluorene, anthracene, 1,2-benzanthracene and 1,2-benzpyrene are shown in Fig. 13. Reference curves for these are omitted from the figure. The fluorene and anthracene curves are obviously completely inadequate for the purpose of precise identification. They are included to illustrate the generalization that a balance of the relevant variables which permits effective resolution on a chromatographic column of some members of the hydrocarbon group is unsuited to the satisfactory resolution of others. Fluorene and anthracene are identified, therefore, with a limited degree of probability, based partly on the spectral characteristics and partly on the position of the fractions in the elution sequence. Sufficient detail is evident in the curves designated 1,2-benzanthracene and 1,2-benzpyrene to establish their identities with a much higher degree of

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probability, although careful examination of both curves would show spectral peaks characteristic of additional hydrocarbons.

The curves of Fig. 12 for coronene are worth detailed remarks. If the activity of the alumina of a column is adjusted to afford a practical degree of resolution of the

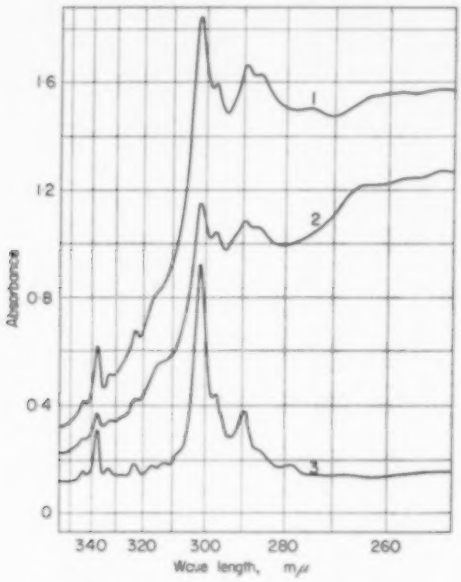

FIG. 12. Ultraviolet spectrograms showing: (1) coronene in urban air sample, (2) coronene in tunnel air sample, (3) reference spectrum for coronene in *cyclo*hexane at 1·0 μg/ml concentration.

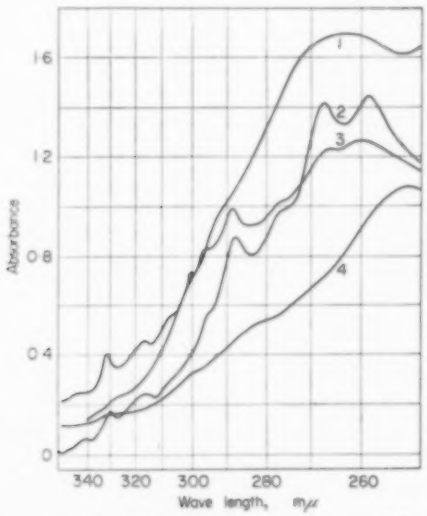

FIG. 13. Ultraviolet spectrograms showing: (1) probable presence of fluorene in urban air sample, (2) 1,2-benzpyrene in urban air sample, (3) 1,2-benzanthracene in urban air sample, (4) probable presence of anthracene in urban air sample.

hydrocarbons preceding coronene in the elution sequence, coronene is elutable only by a considerable volume of an elutant more polar than that used for most of the preceding elution fractions. The spectrograms shown are for fractions eluted with pure benzene. The similarities of the curves for tunnel material and for outside air material are obvious. Comparison of both with the reference curve indicates the presence in the analytical samples of other ultraviolet absorbing material, but structural details coincide well in the three curves. A practical consideration with respect to coronene is that, just as the 335 mμ peak for pyrene serves as an indicator of satisfactory column development, the 302 mμ and 338 mμ peaks for coronene serve as good indicators of the completeness of elution.

The approximate amounts of four polycyclic aromatics in the extract from 478 mg of the particulates collected from Montreal urban air sampling station are shown in Table 2. The calculations include the measurement of peak heights of all working spectrograms which showed well-defined peaks for the hydrocarbons listed, and the values shown are, therefore, greater than can be estimated from the peaks shown in the spectrograms chosen for reproduction.

TABLE 2. APPROXIMATE AMOUNTS OF POLYCYCLIC AROMATIC HYDROCARBONS IN EXTRACT OF 478 mg OF URBAN AIR PARTICULATES

Compound	Approximate amount (μg)	Parts per 100,000 by weight of particulates
Pyrene	11	2·3
Fluoranthene	19	4·0
3,4-Benzpyrene	11	2·3
Coronene	6	1·2

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DISCUSSION

The certainty of identifications based on comparisons of analytical spectra with published spectra or with reference curves prepared from samples of reasonable purity is increased greatly by observation of the elution sequence of the chromatographic fractions to which the curves apply. The chromatography of the organic fraction of air particulates seems to have been established in England as almost a standard routine; the elution sequence of the group of hydrocarbons is known with precision, and this, together with familiarity with the spectral characteristics of the more important hydrocarbons, permits identification with a considerable degree of confidence. In the absence, therefore, of better quantitative methods for the determination of polynuclear aromatic hydrocarbons, the qualified acceptance of data such as those reported by COMMINS seems to be well justified. It is true that more could be desired with respect to sharpness of resolution of the constituent aromatics on the chromatographic column; on the other hand, over-refinement of methods which would effect a needlessly exact determination of hydrocarbons which are not potent carcinogens could scarcely be justified.

These considerations apply to the methods used to analyze the organic fraction of particulates collected from urban air. Their applicability to the same methods when used to analyze for trace amounts of aromatics in tunnel particulates is not so apparent. As shown in the results, only suggestions of characteristic spectral detail

were evident in most of the analytical spectra for tunnel material. The interpretation of slight shoulders and inflections of the curves was frustrating and inconclusive, but in view of the quantities concerned, it is suggested that the elaboration of technique which would be necessary to make the curves more intelligible would not be worthwhile.

The finding of no more than trace indications of aromatics in the tunnel particulates, when considered in relation to the circumstances of sample collection, adds cogency to the conclusion that diesel locomotive emissions contained only very small or inconsequential quantities of aromatics of the kind identified in outside air. Failure to find any traces would have indicated a possible lack of sensitivity in the methods; the finding of small traces is consistent with the assumption, confirmed roughly by the ratios of dust loadings in the atmospheres inside and outside the tunnel, that the particulates collected in the tunnel consisted of about eight or nine parts of diesel emissions to one part of particulates carried into the tunnel by ventilating air.

A conclusion with respect to the practicability of operating diesel locomotives in railway tunnels is that the operation does not occasion exposure of railway personnel to increased concentrations of carcinogenic hydrocarbons of the kind so far identified in urban air. This is substantially in agreement with COMMINS *et al.* (1957) who quote RAFFLE (1957) on the findings of a health study of London Transport staff. For the small number of cases available for study up to 1957, RAFFLE found no increase in lung cancer attributable to the occupational environment of London Transport staff.

A comparison of gaseous concentrations found in the tunnels with those found in bus garages may help to explain the low production of polynuclear aromatics by the locomotives. KATZ *et al.* (1959) found values for total oxides of nitrogen higher than 25 p.p.m. in some instantaneous samples, although the average values for nitrogen dioxide were below the 5 p.p.m. threshold limit of the A.C.G.I.H. COMMINS *et al.* (1957) found in the bus garages values for nitrogen dixoide which were not only below the 5 p.p.m. threshold limit but were of a lower order of magnitude than the concentrations found in the railway tunnels. This comparison suggests that the combustion process characteristic of the large diesel locomotive cylinders favours greater fixation of nitrogen than the combustion in the smaller cylinders of diesel bus motors and, as a corollary, that the oxidation of fuel is more nearly complete in the larger cylinders, with a consequently lower production of condensed ring hydrocarbons.

Diesel locomotives, apparently, do not produce potentially dangerous quantities of a particular group of hydrocarbons. Conclusions with respect to other exhaust constituents cannot, however, be drawn from the results discussed here. More detailed and more general conclusions are given in the main reports of the tunnel studies.

Acknowledgements—Acknowledgement is made to the Canadian National Railways Research and Development Division for the use of tunnel and laboratory facilities with respect to the collection of particulate samples, also to staff of the Occupational Health Division. Thanks are especially due to Mr. J. L. MONKMAN of the Occupational Health Division for making available samples of pure hydrocarbons for reference purposes, and to Mr. BRUCE C. FLANN for the infrared spectra.

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SYMPOSIUM ON POLYCYCLIC HYDROCARBONS

THE CHROMATOGRAPHY OF POLYCYCLIC HYDROCARBONS*

L. DUBOIS, ANN CORKERY and J. L. MONKMAN
Laboratory Services
Occupational Health Division
45 Spencer St.
Ottawa, Canada
(*Received* 22 *October* 1959)

Abstract—A scheme of analysis is presented for pure polycyclic hydrocarbons and extracts of these as found in airborne particulate matter. This is based on preliminary separations of solutions or extracts on columns of deactivated alumina, followed by paper chromatographic separations of individual fractions. For optimum separations the use of acetylated paper has been found essential. Paper chromatography is carried out by the ascending technique as described.

The run is stopped when the solvent front has travelled perhaps 35 cm, and the chromatograms are air dried in an air-conditioned darkroom at constant temperature. The dried paper chromatograms are inspected in the dark under ultra violet light. Zones may be outlined with pencil and R_f values determined. Note is made of the characteristic color of the zones under ultra violet light. Duplicate chromatograms may be sprayed with color developing reagents.

From the R_f values and colors of the sprayed and unsprayed chromatograms preliminary identification can be made. Identification becomes more positive by using ultra violet absorption spectroscopy and ultra violet fluorescence spectroscopy. These techniques are performed on individual spots while still on the paper.

Our experience indicates that separations should be complete before attempting identifications. Separations on acetylated paper are much better than on alumina, although the capacity of paper is much more limited. Certain separations may be made on paper which are practically impossible on a column.

Paper chromatography of the commercially available reagent grades of polycyclic hydrocarbons shows that very few are of adequate purity. It is necessary for workers in this field to purify suitable reagents, preferably to chromatographic standards. Some discrepancies between ourselves and those of other workers with respect to R_f values, colors, etc., may be attributed to materials of uncertain composition.

Reproducibility of R_f values has not been entirely satisfactory. Variation may be as high as $\pm 0{\cdot}03$ R_f units. This lack of reproducibility we believe to be mostly due to variability in the acetyl content of the paper used, from sheet to sheet, and within the sheet. We do find R_f values, however, much more reproducible than R_B values. This is related, in our experience, to the greater variability of the R_f of 3,4-benzpyrene as compared with other hydrocarbons. With almost no exceptions, however, the sequence of separation of a particular group of polycyclics is always the same for a fixed set of operating conditions.

INTRODUCTION

POLYCYCLIC hydrocarbons have been of great interest in connection with air pollution, and certain members of the group are known to be carcinogenic. There seems to be some correlation between lung cancer and highly polluted urban air. This is thought

* Presented before the American Chemical Society, Air Pollution Symposium, 136th National Meeting, Atlantic City, N.J., September 1959.

to be due to the polycyclic hydrocarbon content present in the organic soluble fraction of atmospheric particulate matter. This organic soluble fraction, according to our experience, makes up 10 per cent by weight of the total particulates collected (SUMI *et al.*, 1959). The question is, how much of this 10 per cent is polycyclic in nature or carcinogenic in activity?

Work on the identification of polycyclics found in air samples has been carried out by WEDGWOOD and COOPER (1954; 1955), COOPER (1954), LINDSEY *et al.* (1956), COMMINS (1958a; 1958b), COMMINS *et al.* (1957), KOTIN (1952), KOTIN *et al.* (1954a; 1954b; 1955), SHORE and KATZ (1956) and others. All these workers used column chromatography on alumina, making measurements of the ultra violet absorption of the eluates for identification and quantitative estimation.

Recently there has been a trend towards the use of paper chromatography instead of column chromatography. Work in this field has been done by TEBBENS *et al.* (1956; 1957), THOMAS (1959), THOMAS *et al.* (1957a; 1957b), REUTER (1957), REUTER *et al.* (1958), PIETZSCH (1957) and WIELAND and KRACHT (1957). The paper chromatography of " pure " polycyclic hydrocarbons has been investigated by BERGMANN and GRUENWALD (1957), PIETZSCH (1957), TARBELL *et al.* (1954), GASPARIČ (1958), GASPARIČ and VECERA (1958 and SPOTSWOOD (1959).

Gas chromatography has been applied to the analysis of polycyclic hydrocarbons by DUPIRE (1958), DUPIRE and BOTQUIN (1958), DUPIRE and GRAND'RY (1959), HENDRIKS *et al.* (1957), SOEMANTRI and WATERMAN (1957) and CARRUTHERS *et al.* (1958). WEST *et al.* (1958) analysed a sample of automotive exhaust gas by gas chromatography, obtaining nineteen components none of which was identified. EGGERSTON and NELSEN (1958) show figures for the analysis of engine exhaust and atmospheric samples, by gas chromatography. Their results seem to indicate that the only materials present are low molecular weight paraffins and acetylenes. Apparently no high molecular compounds such as the polycyclics were found. It may be worth mentioning at this point that gas chromatography must be carried out at very high temperatures to have success with the analysis of polycyclics.

Each of the three methods of chromatography mentioned has certain advantages and disadvantages. To avoid being diffuse, emphasis in this paper will be on paper chromatography.

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APPARATUS AND MATERIALS

Paper

The paper chromatography of polycyclic hydrocarbons requires a special acetylated paper. At the beginning we attempted to acetylate ordinary paper with only moderate success. As acetylated paper is now available from Carl Schleicher and Schüll, Dassel, Kreis Einbeck, Germany, we are using the S. & S. material. This paper is sold under the following designations:

2043a	completely acetylated
2043b	acetylated
2045	acetylated
2095	acetylated.

All these papers are available with three different surfaces, mat (m), glazed (gl), and machine finished (mgl). It comes in packages of 100 sheets, 56 × 58 cm. Our experi-

ence has been with the first three varieties, of which we have found 2043b acetylated (mgl) to be the most satisfactory.

Standards

The dry crystalline standards appear reasonably stable in amber glass at room temperature, although *they are better* kept under refrigeration. We prefer to make up standard solutions using spectro grade *cyclo*hexane if possible. For solubility reasons it is sometimes necessary to use toluene as the solvent: as it is desirable not to overload the paper standard concentrations are set up with this in mind. One microgram of polycyclic compound per 1 μl of solution is a usable dilution, but for different hydrocarbons, a solution ten times as strong, or 100 times as dilute may be required.

Micropipettes

To apply standard solutions, or air sample extracts to the paper, we use micropipettes in the capacities 1·0, 2·5, 5·0 and 10·0 μl.

Glass jars

Two circular glass chromatographic jars are used. These are 12 in. in diameter and 24 in. in height, with ground rim and close fitting lid. These will hold a complete sheet of paper stapled in the form of a cylinder.

Chromatographic cabinets

Two chromatographic cabinets of wood and glass are also used. These will hold four to six full sheets of paper each. The wooden frame is impregnated with paraffin wax. On the floor of the cabinet is a long enamel tray to hold developing solvent.

Developing solvents

Basic solvents such as methanol, ethanol, toluene, ether, benzene and chloroform are of reagent grade and anhydrous. They should be checked for the possible presence of fluorescent material before use, and purified further if necessary. The following solvent systems have been used.

Reference	*Solvent system*	*Rate of ascent*
BERGMANN and GRUENWALD (1957)	Toluene–methanol–water 1–10–1	35 cm/24 hr
KRACHT (1958)	Methanol–ether–water 4–4–1	41 cm/24 hr
KRACHT (1958)	Methanol–chloroform 3–1	45 cm/17 hr
SPOTSWOOD (1959)	Ethanol–toluene–water 17–4–1	40 cm/12 hr
SPOTSWOOD (1959)	Ethanol–benzene–water 12–6–1	40 cm/12 hr

The rates of ascent are approximate and intended as a rough guide for the operator.

Ultra violet illumination

A Burton hand ultra violet lamp is used in the darkroom to locate fluorescent zones on the paper chromatogram. This lamp has been modified by the addition of a Kodak 18A ultra violet filter, resulting in light of approximately 3600 Å.

Chromatographic spray reagent

This is a solution of 4·0 g of tetrachlorphthalic anhydride dissolved in a mixture of acetone and monochlorbenzene (100–10) and brought to a final volume of 200 ml (SPOTSWOOD, 1959). This is applied from a glass atomizer using 1–5 lb air pressure. This solution should be made up weekly, and refrigerated when not in use. *Caution*! This spray should be used only in a fume hood with adequate ventilation, as it has been found irritating, and can cause fever and a stubborn bronchial cough.

Densitometer

To make quantitative measurements of zones, a recording densitometer was constructed, having an ultra violet source, simple slit, and sensing head using a cadmium sulphide cell. This can be used to compare relative fluorescent intensities of spots of different materials, or to make quantitative measurements of the spot from the area under the peak.

Recording spectrophotometer

A Perkin Elmer Spectracord Model 4000 is used for ultra violet spectroscopy of solutions or of eluates from a spot. It is also used to obtain ultra violet curves from the paper spot directly, avoiding the need for spot elution.

METHOD

Air samples, being complex mixtures, usually require preliminary extraction, filtration and possibly a simple column separation on alumina to make them amenable to paper chromatography. We extract with *cyclo*hexane, avoiding the use of heat, and completing the extraction as quickly as possible. Exposure to light is avoided as much as possible. Extraction is carried out in 500 ml erlenmeyer flasks or in large beakers, using magnetic stirring. The air sample extract is added to a column of deactivated alumina as recommended by COMMINS (1958a; 1958b). Fractions of 5–10 ml volume are taken arbitrarily, and concentrated to small volume by evaporation in a stream of clean nitrogen.

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A pencil " start " line is drawn near the edge of the paper sheet, at perhaps 1½ in. from the edge, and at right angles to the machine direction of the paper. This line is divided along its length in units of 1 or 1½ in. to serve as centres for the application of samples.

Using a micropipette, standard solutions are applied to the paper in microlitre amounts on the locations marked. Care is taken to hold the pipette at right angles to the paper to avoid distortion. Care is also taken to keep the area of the spot to a minimum. A fan, blowing cool air from below as the spot is applied, is helpful in this. It is wise to run several standard materials on the sheet together with several aliquots of each unknown. This latter is necessary since the concentrations of solutes in an unknown sample is uncertain. Thus, if the larger aliquot (and larger amount of solutes) does not separate well, the smaller aliquot may. It is desirable, also, to leave one or two " tracks " on the paper empty, in case a paper blank is required later.

After the spots are completely dry, the sheet is supported in the cabinet, with the starting line horizontal and downwards, at some distance above the solvent tray. The tray is loaded with 1800 ml of the solvent mixture chosen, the paper is lowered carefully into the solvent, positioned evenly, and supported from a glass rod with stainless steel clips. The depth of immersion and the distance of the start line above the liquid surface are discussed by PIETZSCH (1957).

" Ascending " chromatography is used exclusively since the results obtained are more reproducible than obtainable with " descending ". The chromatogram is run in the dark in a constant temperature room. The run is stopped when the solvent front has travelled a distance of 35 cm.

The sheet is now removed and hung in the dark from a glass rod until completely dry. At this point, we now apply identification criteria in the order following.

(a) Determine R_f value.
(b) Observe colour of spots under ultra violet illumination.
(c) Observe any colour change on spraying with colour developing reagents. Also observe appearance of zones not previously visible.
(d) Determine ultra violet absorption spectra of spots as compared with a paper " blank " cut from an empty track just above the start line of the same sheet.
(e) Determine fluorescence spectra of spots.
(f) Determine ultra violet absorption spectra of eluates of separate spots excised from the paper.
(g) Miscellaneous—There are differences in volatility of spots, densitometric intensities, separation sequences, and associations of spots, which are diagnostic.

It is not intended to convey the impression that the complete routine above must be followed in detail. After application of (a), (b) and (c), the identity of some of the spots may be known. One will almost certainly be able to distinguish fluoranthene, perylene, and benzo-fluoranthene from all the other by R_f and colour alone (a), (b).

After observation of R_f values and colour of spots, selected areas of the sheet may be sprayed to locate " invisible " zones and to differentiate spots further (Tables 1 and 2). It is convenient to run all spots in duplicate, so that when desired a strip 1 in.

TABLE 1. NO COLOUR REACTION WITH TETRACHLORPHTHALIC ANHYDRIDE

Material	Colour
Anthracene	Blue
9-Methylanthracene	Blue
Fluoranthene	Blue white
7,12-Dimethylbenzanthracene	Blue
Perylene	Blue green
3-Methylcholanthrene	Blue
1,12-Benzperylene	Blue
3,4-Benzofluoranthene	Bright blue
3,4-Benzpyrene	Blue
Anthanthrene	Blue
3,4-9,10-Dibenzpyrene	Bright blue

Ultra violet illumination wave length 3600 Å.

to 1½ in. wide may be cut out including one of the " tracks ". This, when sprayed and placed alongside the adjacent unsprayed duplicate track will indicate the position of " invisible " zones.

After spraying, 1,2,5,6-dibenzanthracene, 1,2-benzpyrene, chrysene, fluorene, phenanthrene and triphenyl will be indicated if present. Identification of these substances and those previously mentioned should now be fairly certain using (a), (b) and (c). This involves no expensive instrumentation thus far.

Any zone, whose identity is still doubtful, may be excised and the ultra violet absorption determined as follows. The spot is cut out with scissors as a rectangle of paper perhaps ½ in. × 3/4 in. or somewhat larger. This spot is centred on the cuvette holder window and fastened to it by the edges with cellulose tape. The cuvette holder is then positioned in the usual way with the spot in the sample beam of the spectro-

photometer. Similarly the paper " blank " is positioned in the reference beam. Using a hydrogen lamp source, the spectrum is recorded from 550 to 250 mμ. We disregard the paper graduations, using the chart paper upside down. When prominent peaks are found, the wave length position is noted from the monochromator dial, and recorded on the paper beside the peak (Fig. 1).

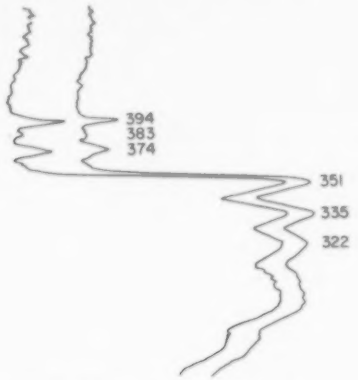

FIG. 1. Ultra violet absorption curves of two dibenzanthracene spots.

With regard to (e), our laboratory does not possess a fluorescence spectrophotometer. Such an instrument, specially designed by Dr. F. R. LIPSETT, was made available to us. With this machine, microgram and submicrogram chromatogram spots could be readily run. This spectrophotometer has certain advantages over commer-

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TABLE 2. COLOUR REACTION WITH TETRACHLORPHTHALIC ANHYDRIDE

Material	Initial colour	Final colour
Acenaphthene	None	Yellow
p-Terphenyl	None	Yellow
m-Terphenyl	None	Yellow
Fluorene	None	Yellow
Phenanthrene	None	Yellow
Pyrene	Violet	Red violet
Triphenylene	None	Yellow
1,2-Benzanthracene	Violet	Red violet
1,2-Benzpyrene	Violet	Orange
6-Methyl chrysene	Violet	Yellow
5-Methyl chrysene	Violet	Yellow
Chrysene	Violet	Bright yellow
1,2,5,6-Dibenzanthracene	Violet	Pink
Coronene	Blue green	Red

Ultra violet illumination wave length 3600 Å.

cially available instruments with regard to sensitivity and selectivity, and samples may be run in vacuum or at reduced temperatures. Fluorescence emission spectra for 3,4-benzpyrene and 1,12-benzperylene are shown in Fig. 2. Here one may note that the fluorescent patterns are very different, although, as already shown, the ultra violet absorption patterns are very similar.

Spots, separated with scissors, may be eluted individually with alcohol, evaporated to dryness in clean nitrogen, and transferred to spectro grade *cyclo*hexane for ultra violet spectroscopy (f). This is less convenient than (d) and should not be used unless (a), (b), (c) and (d) have failed to give unequivocal identification. Elution of the spots

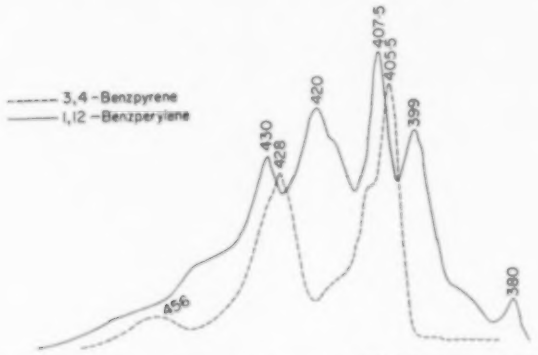

FIG. 2. Comparative fluorescence spectra of 3,4-benzpyrene and 1,12-benzperylene on paper.

is somewhat tedious, recoveries may not be quantitative, and destruction of material may occur.

Referring to (g) it is interesting to note that some spots may be quite volatile. Let us consider an unknown blue spot on a freshly run chromatogram, having an R_f value similar to that of anthracene. We can run the ultra violet absorption curve for the spot, which may show a pattern identical with anthracene. This is likely to be more than sufficient identification. However, if the same spot is run again 24 hr later, and only a rudimentary pattern is now obtained it furnishes further proof that the spot was anthracene.

Having classified and cross-compared our unknown spots according to the procedure just described, we should be able to identify 30 to 40 per cent of the spots in an unknown sample. Identification may, however, fall short of this if either necessary instrumentation, or comprehensive data on standards are unavailable.

RESULTS

The presence of microgram amounts of 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, 3,4-benzpyrene, pyrene, fluoranthene, perylene and chrysene have been demonstrated in Ottawa air. The presence of 1,2-benzpyrene was not observed in numerous air samples tested. On the other hand, small amounts of 9-methylanthracene were found. To our knowledge this material has not previously been reported in air samples. In Table 3 R_f values and separation sequences have been worked out for some of the polycyclic hydrocarbons available to us. We have found perhaps twenty unknown materials in air sample extracts which we have not been able to identify so far. We have encountered problems in the stability and volatility of these materials. Certain discrepancies between our work and that of others have been noted.

TABLE 3. R_f VALUES ON ACETYLATED PAPER S & S 2043b

Acenaphthene	0·88
Fluorene	0·69
Anthracene	0·64
Phenanthrene	0·62
9-Methylanthracene	0·57
Pyrene	0·52
Fluoranthene	0·51
1,2-Benzanthracene	0·43
1,2-Benzpyrene	0·41
Perylene	0·28
Chrysene	0·22
1,12-Benzperylene	0·18
1,2,5,6-Dibenzanthracene	0·16
3,4-Benzpyrene	0·10
Anthanthrene	0·07

DISCUSSION OF RESULTS

We do not wish to give the impression that the separation and identification of polycyclic hydrocarbons is now a completely routine matter. As previously mentioned, in air samples, unknown substances exceed the known by a considerable margin. To some extent, of course, this is due to the lack of data on standards, which could be used to compare with the unknowns. This is a serious situation which bedevils numerous analytical techniques such as X-ray diffraction, ultra violet absorption and infra red absorption, to mention some of the techniques which come to mind. This awkward gap might be made smaller if systematic efforts were made by all concerned to tabulate and distribute such useful data on all pure polycyclics which can conceivably be found in air.

Even among practising chemists it may not always be realized how easy it can be to make the wrong interpretation from data available. Ultra violet absorption spectroscopy, as previously applied to air samples was essentially the measurement of the properties of mixtures, not pure substances, since eluate fractions taken from a column are not, in real life, cleanly separated with respect to the dissolved solutes. This is illustrated in Table 4.

From this table it may be seen that a mixture in solution of 3,4-benzpyrene and 1,12-benzperylene does not separate on an alumina column. If we apply the analytical

TABLE 4. COMPARATIVE SEPARATIONS ON ALUMINA AND PAPER

Materials	Column	Paper
Anthracene–phenanthrene	None	Partial
Anthracene–pyrene	Poor	Complete
Pyrene–fluoranthene	None	None
Fluoranthene–1,2-benzanthracene	Poor	Complete
1,2-Benzanthracene–3,4-benzpyrene	Poor	Complete
1,2-Benzanthracene–1,2-benzpyrene	Poor	Complete
3,4-Benzpyrene–1,2-benzpyrene	None	Complete
3,4-Benzpyrene–1,12-benzperylene	Poor	Complete

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method of COMMINS (1958a; 1958b) to an unknown mixture which might contain these two components, there are many opportunities for error. COMMINS looks for a diagnostic peak at 403 mμ. This peak is certainly very characteristic of benzpyrene and is not shown by benzperylene. However, between 403 mμ and 312 mμ there are five more peaks which are " common " to benzpyrene and benzperylene. A mixture of the two, then, could be readily diagnosed as consisting only of benzpyrene (Fig. 3),

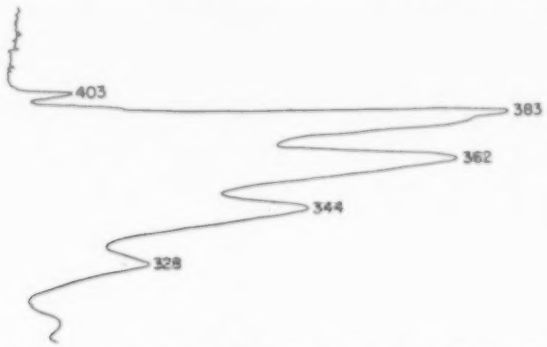

FIG. 3. Comparative ultra violet absorption spectra of 3,4-benzpyrene and 1,12-benzperylene in *cyclo*hexane solution.

even assuming these six peaks were all present. On our spectrophotometer, one ordinarily records from 375 to 200 mμ. Thus there may be a tendency for the analyst to be conditioned by the instrument to neglect wave lengths above 375 mμ. We avoid this pitfall by using plain paper in the instrument and starting to scan at 550 mμ.

However, in the region of low concentrations which may occur in extracts from air samples, it is possible to have equal concentrations of these two polycyclics with the 403 peak completely absent due to the low concentration (Fig. 4).

Confronted with the evidence of such a pattern we can only hope that the analyst will be discriminating, and admit the three possibilities, namely (1) benzpyrene, (2) benzperylene or (3) both. He might then, with advantage, run a paper chromatogram of the solution.

Similar ambiguities apply to the u.v. absorption spectra of chrysene and 6-methyl chrysene (FRIEDEL, 1956), and benzanthracene and fluoranthene (COMMINS 1958a; 1958b). Many other instances of this kind could be cited.

The essentially poor separations achieved by an alumina column make it necessary for COMMINS to use simultaneous equations to determine fluoranthene and benzanthracene in the presence of one another. Referring to Table 4, we see that although column separations tend to be incomplete, by contrast separations on paper are sharp and clear-cut for amounts not exceeding the capacity of the paper. For instance, it is rather easy to separate 3,4-benzpyrene from 1,12-benzperylene, and fluoranthene from benzanthracene, on acetylated paper. Having achieved such a separation of any of these polycyclics, excision and elution of the spot, with subsequent u.v. absorption analysis, will give an unequivocal confirmation of identity, which was not possible while the extract was a mixture. The identity of fluoranthene would probably be fairly certain without elution and u.v. analysis of the eluate, since its colour on paper is distinctively different from most of the hydrocarbons.

From what has been said, it should be fairly clear that the identification of polycyclics is partly, if not largely, a question of separations. Now that good separations of individual polycyclics can be achieved, such a separation should always be a part of the analysis. Without compelling reasons, instrumental analysis should not be attempted on any sample, either solution or paper spot, unless prior separation has isolated one component. Instruments can only give back to the analyst as much

FIG. 4. Comparative ultra violet absorption spectra of 3,4-benzpyrene and 1,12-benzperylene in *cyclo*hexane solution.

information as he has built into it through his sample preparation and care spent in making careful separations will repay the analyst with data in which he can have confidence.

Paper chromatographic separation and identification of standard polycyclics or mixtures thereof is relatively easy, since the complexity of the system analysed is under the control of the analyst. Air samples are much more complex and preliminary separations and elimination of background absorption, is therefore more important. For such samples, it is often helpful to make a rough and arbitrary fractionation of the sample on an alumina column. The separate fractions may be concentrated by evaporation under nitrogen, and then each fraction run as a separate track on the paper chromatogram. Such a twofold separation of an air sample is shown in Fig. 5 The complexity of the sample is evident.

After a paper chromatogram has been prepared, the first obvious step is to inspect it under ultra violet illumination. The observed colour of individual hydrocarbons will depend upon the wave length of the illuminating light. The light must be adequately filtered so that only ultra violet reaches the chromatogram. In our case, we use a second filter, Kodak 18A, over the lamp, which peaks at 3600 Å and cuts off above 4000 Å. Unless the illumination used is of this character, another observer might consider the colours somewhat different than those described by us.

Aside from the character of the illuminant, there may be subjective differences in

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the colours as seen by different analysts. We find it hard to accept, however, the classification given by GASPARIČ (1958) for pyrene, fluoranthene and 3,4-benzpyrene, namely " bright blue ". The three are distinctly different in colour, and cannot be classified as similar. He also finds dibenzanthracene to be " yellow ", against our violet.

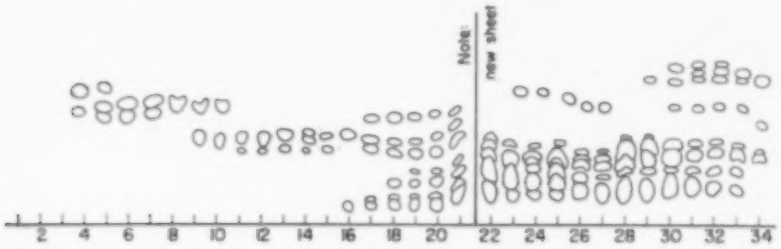

FIG. 5. Paper chromatogram of composite air sample. Preli minary separation by chromatograph on partially deactivated alumina. Each column fraction a separate track on paper chromatogram.

In Table 2 " none " is to some extent a relative term. Considering phenanthrene of paper chromatographic purity, we have been unable to see a zone containing 20 μg or less of the hydrocarbon. Quantities larger than this may barely be distinguished. However, as this exceeds the amounts usually run on paper, it is possible that others may not have seen phenanthrene for this reason. GASPARIČ (1958) classifies phenanthrene as " weak violet ", SPOTSWOOD (1959) states colour under ultra violet light to be " none ", WIELAND and KRACHT (1957) indicate no colour, and KRACHT (1958)

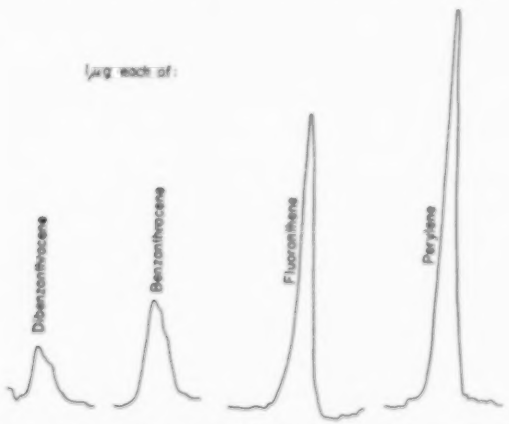

FIG. 6. Comparative ultra violet densitometric intensities for identical amounts of four hydrocarbons.

considers it " deep dark violet ". KRACHT, and WIELAND and KRACHT, use u.v. light wave length 2540 Å; the exact wave length of light used by GASPARIČ and SPOTSWOOD is not certain.

As noted by PIETZSCH (1957), polycyclic hydrocarbons can be classified in order of intensity of fluorescence, on the paper chromatogram. Fig. 6 is a densitometer tracing of 1 μg of each of four hydrocarbons on a paper chromatogram. As may

be seen, the peak height is much greater for the strongly fluorescing materials.

The actual colour of the fluorescent spot seems also to be related, at least in the case of fluoranthene, to the amount of material present. Thus larger amounts of fluoranthene are blue white, and smaller amounts yellow green, in our judgment. In this we

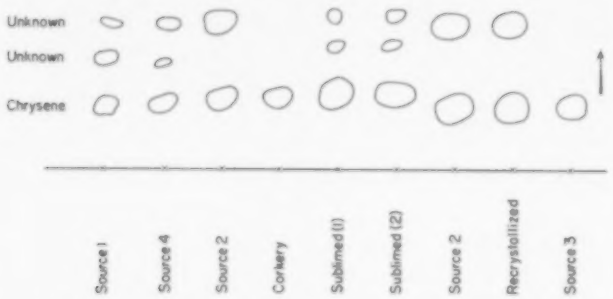

FIG. 7. Paper chromatographic separation of various chrysene preparations.

seem to be in agreement with KRACHT, who gives two colour shades for fluoranthene without comment, " blue white " and " yellow green ".

Naturally, the colour observed may depend on the purity of the material. Thus, for example, is chrysene, " colourless " or " deep dark violet "? In our experience samples of chrysene from various sources invariably yielded three spots on a paper chromatogram. These three spots are all visible under ultra violet light if sufficient material is present, although the intensities are different.

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FIG. 8. Comparative ultra violet absorption curves for chrysene zones 2 and 3 on paper.

Spot 1 (highest R_f) remains unchanged in colour after spraying, spots 2 and 3 both become bright yellow. By recrystallizing " chrysene " from hot toluene one obtains a product which lacks zone 2 on chromatographing. These components of chrysene are illustrated in Fig. 7. In brief, by eluting spot 3, a preparation may be obtained which yields only one spot on repeated chromatography. The u.v. absorption curves for this material match curves in the literature for chrysene (see Fig. 8). From this, and other evidence, we have concluded that spot 3 is chrysene, spot 2 is probably a

methyl chrysene, and spot 1 is another unknown. We think what we have said about chrysene will explain why colours and R_f values of a particular hydrocarbon can be the subject of confusion.

As analysis of these hydrocarbons must ultimately depend on comparison with pure standards, the fact that the standards available are usually quite impure is a serious hindrance. In Fig. 9 may be seen a chromatogram of three separate samples of

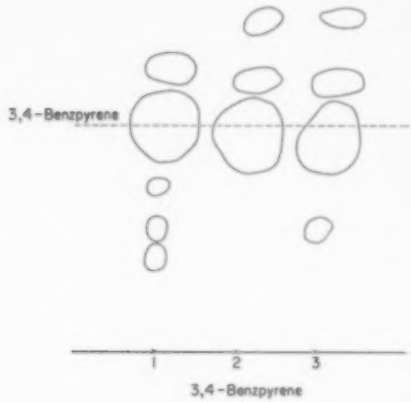

FIG. 9. Paper chromatogram of three separate samples of 3,4-benzpyrene standard from the same supplier.

3,4-benzpyrene all received from one supplier under the same catalogue number. It is evident that each sample is somewhat different. Similarly, Fig. 10, a chromatogram of perylene, indicates the impurity of this material.

In Table 3 are shown R_f values of microgram amounts of fifteen hydrocarbons. These values are based on ascending chromatography on acetylated paper using the

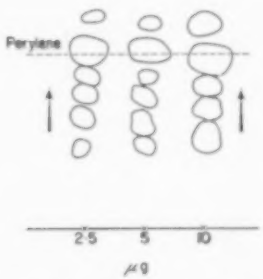

FIG. 10. Paper chromatogram of perylene standard showing associated impurities.

solvent system toluene–methanol–water 1–10–1. No claim is made for the absolute accuracy of these R_f values, but the separation sequences are completely reproducible under our conditions. A reasonable separation can be expected if the values differ by 0·05 R_f units, and sometimes if the R_f difference is less. Separations suffer, of course, if the paper is overloaded.

All the hydrocarbons listed separate well, with some exceptions. The isomers pyrene–fluoranthene do not separate. However, some of the isomers in the table do

separate well, namely 1,2-benzpyrene–perylene–3,4-benzpyrene, and 1,2-benzanthracene–chrysene. Separation of 1,2-benzanthracene and 1,2-benzpyrene is good, although the R_f difference shown is only 0·02 units. All hydrocarbons were run many times with the system described before entering in this table. Other hydrocarbons investigated but not included in this table were coronene, 3,4-9,10-dibenzpyrene, 3,4-benzofluoranthene, 3-methylcholanthrene and 7,12-dimethylbenzanthracene. With further work it is hoped to fit these into the tabulation as well.

On occasion, the isomers anthracene–phenanthrene may not separate completely. Clearly separated spots are illustrated by the paper spot spectra shown in Fig. 11. A spot where separation is incomplete is shown in Fig. 12. Assuming such a " mixed " spot is visible under ultra violet light, it may consist of anthracene, or anthracene plus phenanthrene. It will not be phenanthrene alone. If, on spraying with tetrachlorph-

FIG. 11. Ultra violet absorption spectra on paper of separate spots of anthracene and phenanthrene.

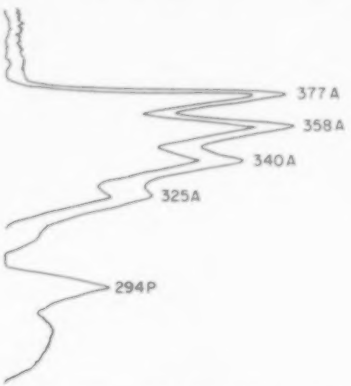

FIG. 12. Ultra violet absorption spectra on paper of a mixed spot containing both anthracene and phenanthrene.

thalic anhydride, the spot remains unchanged in colour, phenanthrene is absent, and the spot consists only of anthracene. A spot which contains both components will change colour to yellow on spraying.

A spot which may consist of both pyrene and fluoranthene can be interpreted to some extent by comparison with spots of the two separate pure components. Since these two substances are very different in colour it is not too difficult to decide whether both are present in one spot. As the fluorescence intensity of fluoranthene is much greater than that of pyrene, mixed spots are more likely to resemble fluoranthene in appearance, than pyrene. As both pyrene and fluoranthene are commonly encountered in air samples, the need for a good separation of these two is obvious.

We have found it difficult to reproduce R_f values on acetylated paper. This is at least partly due to differences in the behaviour of the paper from sheet to sheet. Admitting this, and even allowing for certain differences in paper and procedure from one laboratory to another, we believe BERGMANN and GRUENWALD (1957) to be incorrect in assigning an R_f value of 0 to chrysene. In our experience chrysene, and any associated impurities, have R_f values between 0·2 and 0·3, with nothing left at the start line.

Since the R_f values we originally obtained seemed quite variable, we also calculated

the corresponding R_B values (WIELAND and KRACHT, 1957) for each hydrocarbon in the hope that these latter values might prove more reproducible. We found, in fact, over a long period of time and after many determinations, that R_f values were more dependable than R_B values. This, we think, from our experience is related to the higher inherent variability of the R_f value of 3,4-benzpyrene, which is the denominator of the R_B value. Also, since the R_f value of 3,4-benzpyrene is one of the smallest values encountered it is not measurable with the same degree of accuracy as the R_f of fluoranthene for example. We would like to suggest that an " R_B " value based on the R_f value of fluoranthene might be worth investigating. We suggest fluoranthene, since the R_f value is fairly large, the compound seems fairly stable, the colour is distinctive, and the reproducibility of R_f values has always been good in our experience.

The accuracy of identifications and quantitative estimations of polycyclic standards, and polycyclics isolated from air samples is affected by many factors including, in the

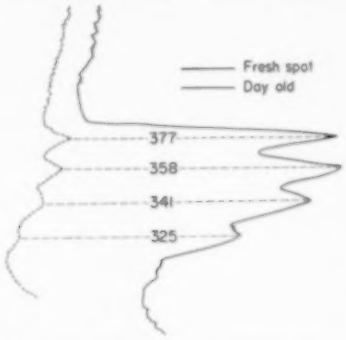

FIG. 13. Ultra violet absorption spectra of authracene spot illustrating the volatility of this material on the chromatogram.

case of air samples, breakdown during extraction, and incomplete extraction. Oxidation, exposure to ultra violet light and heat all have adverse effects on the micro amounts involved. It is likely, therefore, that quantitative figures in the literature are low.

We find that microgram amounts of many polycyclics on a paper chromatogram are unstable. There is an observable tendency for spots to fade with time. Spots will also migrate from the dry paper chromatogram to another surface such as a paper sheet with which it may be in contact for a short while. Fig. 13 illustrates the volatility of an anthracene spot after 1 day's exposure to ordinary laboratory conditions. Anthracene may be considered perhaps one of the worst actors in this regard. It is, however, possible to arrest this " evaporation " from the paper by keeping spots of particular interest in 5×7 film holders and storing in a refrigerator. Spots handled in this way do not lose intensity. Standard solutions also deteriorate with time even although stored in a refrigerator when not in use. This instability is not as serious as it might seem, as long as one realizes it is a factor and allows for it.

CONCLUSIONS

We have endeavoured to set forth a general scheme of analysis of polycyclic hydrocarbons. This depends on complete, or nearly complete, paper chromatographic separation before identification. In addition to R_f value, and colour under u.v., the

ultra violet absorption of paper spots and eluates of paper spots are useful. If suitable equipment is available, fluorescence spectra of the paper spots can be obtained. These are more definitive than the u.v. spectra obtained from the same spot. Identification must be based on as many criteria as possible, at least four of those mentioned. Supplies of pure standards are urgently needed. Exhaustive compilation of data for identification based on pure standards is essential.

Acknowledgement—The authors wish to thank B. T. COMMINS, B. L. VAN DUUREN, R. A. FRIEDEL, M. S. NEWMAN and TH. WIELAND for gifts of polycyclic hydrocarbons. Thanks are also due to F. R. LIPSETT through whose courtesy fluorescence spectra were determined.

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SYMPOSIUM ON POLYCYCLIC HYDROCARBONS

ULTRAVIOLET, VISIBLE AND FLUORESCENCE SPECTRAL ANALYSIS OF POLYNUCLEAR HYDROCARBONS*

E. SAWICKI, T. R. HAUSER and T. W. STANLEY
Air Pollution Engineering Research,
Robert A. Taft Sanitary Engineering Center,
Public Health Service,
U.S. Department of Health, Education, and Welfare
Cincinnati 26, Ohio
(*Received* 23 *July* 1959)

Abstract—A novel approach to the analyses of polynuclear hydrocarbons in mixtures is introduced. On the basis of this approach a new simple, sensitive and specific test for benzo[*a*]pyrene has been developed. In a mixture of fifty compounds containing benzene, naphthalene, anthracene, phenanthrene, benz[*a*]anthracene, benzo[*c*]phenanthrene, chrysene, pyrene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, perylene, benzo[*g,h,i*]perylene, anthanthrene and coronene, benzo[*a*]pyrene can be identified unequivocally. The ultraviolet-visible, activation, and fluorescence spectra in pentane of a large number of polynuclear hydrocarbons are presented. The fluorescence intensities of the different hydrocarbons are compared. Some, like anthanthrene and perylene, have an extremely high intensity, which simplifies their detection in a mixture. The sensitivity of the fluorometric methods are of the order of millimicrograms per milliliter, or parts per billion. From a comparison of the activation spectra in pentane and sulfuric acid of different hydrocarbons, it can be ascertained whether a given hydrocarbon can be determined in the presence of hydrocarbons of somewhat similar structure. In many instances it is possible to obtain the pure fluorescence spectrum of an aromatic hydrocarbon by determining the spectrum of the mixture at an appropriate activation wavelength maximum of the aromatic hydrocarbon. Thus benzo[*e*]pyrene can be determined in the presence of benzo[*a*]pyrene, and vice versa. Perylene or anthanthrene can be detected readily in a complicate mixture of some twenty-five analogous hydrocarbons. Naphtho[2,3-*a*]pyrene can be detected in a mixture of fifty polynuclear hydrocarbons. Many other possibilities are apparent from an examination of the activation spectra of the hydrocarbons. The quenching effect of a fairly high concentration of miscellaneous compounds in a mixture as it affects fluorometric analysis for some particular hydrocarbons is also discussed.

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SIMPLE, specific and sensitive methods for the detection and determination of polynuclear hydrocarbons can be of great value in properly evaluating the human environment, especially since some of these hydrocarbons are thought to be carcinogenic agents (HADDOW and KON, 1947). Recently several general methods have been developed for the analysis of polynuclear compounds (SAWICKI and BARRY, 1959; SAWICKI *et al.*, 1958a; SAWICKI *et al.*, 1958b). Although these general methods are fairly sensitive, their specificity for the determination of any one particular hydrocarbon in a mixture is very poor. The principal method of analysis for polynuclear hydrocarbons in air particulates, tobacco smoke, tar, etc., has consisted of chromatography followed by ultraviolet (COOPER, 1954; KOE and ZECHMEISTER, 1952; KOTIN *et al.*, 1954) or fluorescent spectral analysis (WALLER, 1952).

* Presented before the American Chemical Society, Air Pollution Symposium, 136th National Meeting, Atlantic City, N.J., September 1959.

The ultraviolet spectral method is based on the fact that the polycyclic hydrocarbons have sharp characteristic absorption peaks which (in the case of the prominent peaks) usually protrude above the background absorption of the mixture. The position of the bands of a particular hydrocarbon is believed to be unaffected by the presence of other hydrocarbons. The amount of a polynuclear hydrocarbon in an eluted fraction can be determined by measuring the height of a peak above a base line formed by drawing a line between two definite wavelengths on either side of the peak. The peak heights for each polycyclic hydrocarbon are measured and compared with those obtained from solutions containing known amounts of pure hydrocarbon (COMMINS, 1958; COOPER, 1954). The presence of other chemicals containing a band close to the peak of the hydrocarbon being analyzed interferes with the accuracy of this method. For the identification of a hydrocarbon, the individual fractions are usually re-chromatographed many times to obtain a fairly pure sample which can then be identified by spectral comparison with the pure hydrocarbon. This procedure is tedious and practically impossible if only a small amount of sample is available.

In the past, fluorometric analysis has been plagued by quenching effects, instrumental difficulties and poor specificity. Nevertheless, with modern fluorescence instrumentation, the joint use of chromatography, ultraviolet spectrometry and fluorometry makes possible a more thorough investigation (VAN DUUREN, 1958). However, the full potentiality of fluorometric analysis has never been completely explored. In this paper we hope to show some of the exciting techniques available to the analyst in this field.

EXPERIMENTAL

Reagents and equipment

Pentane (Laboratory Services, Inc., Cincinnati 9, Ohio) was distilled and the middle fraction, boiling at 35–36°, was collected.

The polynuclear hydrocarbons were obtained from Aldrich Chemical Co., Inc., Milwaukee 12, Wisconsin, and K and K Laboratories, Inc., Jamaica 33, New York. Coronene and benzo[*c*]phenanthrene were obtained from Dr. M. S. Newman.

Mixture *A* consists of the following compounds: benzene, naphthalene, anthracene, 9-methylanthracene, phenanthrene, acenaphthene, fluoranthene, triphenylene, 4-*cyclo*penta[*d,e,f*]phenanthrene, 11-benzo[*a*]fluorene, 11-benzo[*b*]fluorene, 7-benzo[*c*]-fluorene, chrysene, pyrene, 1-methylpyrene, 4-methylpyrene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*e*]pyrene, dibenz[*a,h*]anthracene, benzo[*b*]fluoranthene, picene, benzo[*c*]phenanthrene, benzo[*g,h,i*]perylene and coronene. The stock solution in pentane is 10^{-3}M for each hydrocarbon.

Mixture *B* consists of the above hydrocarbons (except benzo[*a*]pyrene) and the following: toluene, durene, diphenylmethane, mesitylene, biphenyl, *o*-terphenyl, *m*-terphenyl, *p*-terphenyl, *p*-quaterphenyl, phenyl ether, phenyl sulfide, fluorene, 2-methylfluorene, 2-ethylfluorene, dibenzofuran, dibenzothiophene, 9,9′-difluorenyl, 2-methylphenanthrene, 3-methylphenanthrene, 9,10-dimethylbenz[*a*]anthracene, 3-methylcholanthrene, benzo[*k*]fluoranthene, perylene and anthanthrene. The stock solution in pentane is 5×10^{-6}M for each hydrocarbon. The total concentration of this mixture is 51 μg of hydrocarbons per milliliter. The sulfuric acid solutions of *A* and *B* were freshly prepared by evaporating an appropriate volume of the stock solution at room temperature and diluting to the mark in the appropriate volumetric flask.

A Cary recording quartz spectrophotometer, Model 11, was used for absorption wavelength determinations; an Aminco–Bowman spectrophotofluorometer was used for the determination of activation and fluorescence spectra. One centimeter cells were used throughout the study. Thermo-Vac ovens (Schaar and Company, Chicago 34, Illinois) were used for evaporation of pentane solutions at room temperature in the dark under a vacuum.

Procedure

Fluorescence spectra are reported at the most intense activating wavelength of a compound, activation spectra at the most intense fluorescence wavelength. All spectra have been determined in pure pentane unless otherwise stated. The following settings were used in the spectrophotofluorometer: the sensitivity was set at 50; slit arrangement No. 2 (where the narrowest slit width is 1/32 in.) and phototube RCA Type 1P21 (see American Instrument Co., Instructions Manual No. 656) were used. The maximum sensitivity of the phototube occurs at 500 mμ. Many slit arrangements are possible with this instrument. Those involving smaller slit widths give greater resolution. With larger slit widths, the sensitivity is greater, but so is the background noise. Hence, for analytical work, the analyst must compromise to obtain the most suitable combination for his particular procedure. In all fluorometric work, the activation and fluorescence wavelengths and intensities obtained on the instrument should be checked daily with a standard solution. In our laboratory we have used a 1 μg/ml solution of quinine in 0·1N sulfuric acid and a 10^{-6}M solution of benzo[*a*]-pyrene in pentane as standards.

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DISCUSSION OF RESULTS

Pentane is probably the ideal solvent for the analytical investigation of mixtures containing polynuclear hydrocarbons (2–6 fused rings), especially with column chromatography and ultraviolet, visible and fluorescence spectral analyses. The advantages of pentane are:

(a) it is easily purified;
(b) it readily dissolves pentacyclic (and smaller) aromatic hydrocarbons and many hexacyclic hydrocarbons;
(c) with the addition of ether, a more powerful eluting solvent is at hand for chromatographic separations;
(d) it is easily and quickly evaporated at room temperature under a vacuum, giving a minimum of decomposition and facilitating further analysis;
(e) it has a low ultraviolet cutoff, and
(f) it has a very low blank in fluorescence analysis.

The ultraviolet-visible absorption spectra in pentane of a large group of hydrocarbons have been determined (Table 1). Such a collection has value because the peaks of any one hydrocarbon are at exactly the same position in the spectrum of a mixture or of a pure solution ($\pm$ 1 mμ) as long as the same solvent is used. By means of these peaks, aromatic hydrocarbons can be tentatively identified and in some cases even be estimated. Examples appear later in the paper.

Fig. 1 shows the activation spectrum of benzo[*a*]pyrene as obtained with the spectrophotofluorometer, and the absorption spectrum as obtained by any standard spectrophotometer. The activation spectrum has less fine structure than the absorption spectrum, although the relative intensity of the peaks in any one band system are

TABLE 1. ULTRAVIOLET ABSORPTION SPECTRA OF POLYNUCLEAR HYDROCARBONS IN PENTANE

Acenaphthene		Fluorene		Anthracene		9-Methylanthracene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~228	27·5	255	17·4	~221	11·0	~223	14·0
244	1·4	261	18·5	246	112·0	249	105·0
258S	2·0	264S	18·0	252	210·0	256	213·0
268S	3·8	272	13·0	290S	0·7	302S	0·56
278	5·8	289	6·7	308	1·4	316	1·24
281S	5·6	294	5·4	322	3·0	331	2·96
289	6·6	300	9·2	334S	4·3	347	6·20
293S	5·4			338	5·7	365	10·2
300	4·0			351S	5·7	384	9·72
306	2·4			355	8·7		
310	1·0			368	4·0		
314	0·86			374	8·7		
316	0·79						
321	1·58						

Phenanthrene		2-Methyl-phenanthrene		3-Methyl-phenanthrene		4-*Cyclo*penta[*d,e,f*] phenanthrene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~221	22·0	~223	25·0	~224	22·0	~223	28·0
244	51·0	245S	55·0	246	50·0	226	25·0
251	69·0	253	77·0	253	64·0	250S	50·0
258S	30·0	267S	16·6	266S	14·7	252	57·0
264S	14·5	272	14·7	270	14·0	262	18·6
267S	12·9	278	15·7	277	14·5	268S	10·3
275	14·2	284	12·2	284	11·1	271S	9·0
281	11·2	296	12·2	296	14·4	276	9·3
290S	7·0	312S	0·21	311	0·34	279S	8·1
293	14·8	318	0·24	318	0·38	284S	8·8
310	0·21	325	0·23	326	0·35	288	12·5
314S	0·22	332	0·23	333	0·51	290S	7·9
317	0·25	341	0·21	340	0·28	297	10·0
324	0·28			349	0·52	300	16·1
331	0·30					314	0·42
339	0·27					323	0·27
347	0·26					330	0·56
						334	0·34
						340	0·19
						346	0·57

TABLE 1. ULTRAVIOLET ABSORPTION SPECTRA OF POLYNUCLEAR HYDROCARBONS IN PENTANE (*continued*)

Fluoranthene		Pyrene		1-Methylpyrene		4-Methylpyrene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
230S	34·6	231	44·0	234	48·0	233	47·0
235	52·6	237S	57·2	244	100·0	242	88·0
243S	18·6	240	89·6	254	19·0	254	14·0
248S	15·8	252	11·6	264	35·0	264	28·0
252	15·6	261	26·0	275	59·0	274	51·0
258	13·2	272	53·2	295	14·0	294	6·0
262	14·8	293	4·4	307	16·0	307	14·0
264S	10·6	305	11·2	321	22·0	321	32·0
271	13·0	318	30·0	332S	25·0	332S	26·0
276	26·5	330S	22·8	336	57·0	337	54·0
281	20·0	334	54·8	355	0·58	352	0·59
287	50·8	351	0·48	359	0·31	358	0·32
309	3·76	357	0·34	364	0·31	363	0·33
323	6·44	361	0·33	369	0·21	372	0·19
341	8·2	365S	0·20	373	0·25		
351S	6·4	371	0·13				
358	8·76						

11 H-benzo[*a*] fluorene		11 H-Benzo[*b*] fluorene		7 H-Benzo[*c*]fluorene		Benz[*a*] anthracene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~222S	24·4	~220S	33·0	230	51·2	~222	47·0
229	22·4	225S	27·0	240S	30·4	227	43·0
238	18·0	237	20·0	251	17·4	242S	28·0
244	24·4	245	25·0	262	6·5	250S	39·0
253	58·0	254	51·0	268	4·7	255	40·0
257	44·0	263	73·0	277S	4·7	267	47·0
262	98·8	273	14·8	290S	8·0	276	83·0
274	9·9	285	13·0	299	12·2	287	101·0
286	12·2	290	9·7	302	12·2	297S	8·8
294	13·8	303	17·7	311	16·4	299	10·0
303	15·4	312S	13·1	314	15·6	314	4·9
312S	12·1	316	22·9	322	14·2	325	6·9
316	15·3	325	7·7	329	12·7	340	7·9
324	3·0	328S	2·8	336	18·5	358	5·5
329	2·1	332	3·0			364	2·5
331S	1·6	340	8·7			374	0·6
336	1·0	348	0·12			382	1·0
340	2·7						
345	1·1						

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TABLE 1. ULTRAVIOLET ABSORPTION SPECTRA OF POLYNUCLEAR HYDROCARBONS IN PENTANE (*continued*)

7,12-Dimethylbenz[*a*]anthracene		Chrysene		Triphenylene		5,12-Dihydrotetracene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~222	29·0	241	20·0	240S	40·0	~228	160·0
235	17·0	249S	33·0	249	91·0	247	2·7
254S	23·0	257	79·0	258	162·0	252	3·1
263	30·0	267	154·0	275	18·2	259	4·2
274	33·0	282	12·7	286	16·9	268S	5·2
285	64·0	294	12·4	302	1·7	271	5·8
296	78·0	306	13·6	313	0·34	279	5·3
330S	3·4	320	13·8	321	0·39	289	3·6
347	6·1	333S	0·47	328	0·26	305	0·90
362	8·2	343	0·55	335	0·33	315	0·50
380	6·0	350	0·33			320	0·80
		352	0·35				
		360	0·60				

Benzo[*b*]fluoranthene		Benzo[*k*]fluoranthene		Benzo[*a*]pyrene		Benzo[*e*]pyrene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~222	42·0	237	64·0	~226	28·0	236	29·0
239	38·0	247	60·0	254	39·2	256	24·8
245	37·0	268	27·0	265	47·2	266	30·6
256	44·0	283	29·0	271	28·8	277	42·4
261S	38·0	296	50·0	283	44·4	289	58·4
271S	26·0	308	71·0	296	60·8	302	13·4
276	31·0	321S	7·8	313	3·6	305	13·4
281S	27·0	336S	5·2	330	5·4	316	24·2
289	31·0	341	5·0	345	13·2	320S	14·8
293	31·0	352	3·5	362	25·8	327S	18·2
302	49·0	358	7·3	377	27·6	331	38·6
336S	10·6	370	6·0	379	27·2	348	0·54
342	11·2	377	17·0	382	30·5	356	0·33
350	11·4	383S	5·6	391	4·1	358	0·34
358S	8·7	392	7·1	401	4·2	365	0·54
367	7·4	401	21·9				
391	0·34						
401	0·47						

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA OF POLYNUCLEAR HYDROCARBONS IN PENTANE (*continued*)

Perylene		3-Methyl-cholanthrene		Benzo[*b*]chrysene		Dibenz[*a*,*c*] anthracene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~226	18·0	~223	34·0	~229	71·0	230	66·0
238S	16·6	237	30·0	242S	35·0	238S	37·0
244	34·8	256S	33·0	247	35·0	247	36·0
252	46·0	262	38·0	250S	34·0	253	32·0
262	9·8	274	39·0	255S	29·0	257	33·0
291	1·4	285	74·0	264	32·0	264	50·0
365	4·4	290S	58·0	275	81·0	274	99·0
385	12·2	297	98·0	279	82·0	286	140·0
406	26·8	305	22·9	286	148·0	307	8·5
410S	24·8	328	4·7	297	46·0	322	8·3
429	29·6	343	7·3	302	49·0	332	6·7
434	36·6	360	8·7	318a	7·0	349	3·0
		373S	5·5	331a	8·0	354S	1·6
		380	6·0	344a	9·0	364	0·3
		392	3·8	347a	9·0	373	0·5
				361a	10·0		
				368a	7·0		
				380a	7·0		
				388a	5·0		

Dibenz[*a*,*j*] anthracene		Dibenz[*a*,*h*] anthracene		Picene		Anthanthrene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~224	94·0	~222	63·0	~226S	13·0	234	88·4
230S	64·0	232	27·0	236S	18·0	242S	39·2
241	26·0	241	6·0	248S	33·0	246S	30·8
246	28·0	264S	19·0	256	44·0	255	32·0
250	29·0	274	47·0	265S	40·0	258	37·6
257	38·0	278	46·0	274	67·0	271	5·2
263	14·0	286	95·0	284	103·0	283S	11·6
267	14·0	288S	90·0	301	29·0	294	38·8
274	31·0	297	184·0	312	15·0	307	84·8
285	79·6	308S	22·0	326	20·0	321S	6·4
297	137·0	321	19·8	358	0·8b	365S	3·2
300S	85·0	333	17·4	364	0·45b	374S	7·6
308S	21·0	344S	8·7	375	0·79b	378	12·8
321	17·1	348	15·8			382	12·4
334	14·3	362	0·5			393S	18·0
337	14·4	372	0·9			399	32·0
342S	4·5	381	0·4			405	34·0
348	5·9	391	0·9			414	15·6
363S	~ 0·47b					420·5	56·0
373	~ 0·58b					429	70·4
383	~ 0·31b					434S	6·4
393	~ 0·33b						

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TABLE I. ULTRAVIOLET ABSORPTION SPECTRA OF POLYNUCLEAR HYDROCARBONS IN PENTANE (*continued*)

Coronene		*o*-Phenylene pyrene		Dibenzo[*a*,*e*] pyrene		Naphtho[2,3-*a*] pyrene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~251	8·0	~228	78·0	~222	74·0	239S	30·5
267	8·0	241	50·0	230S	38·8	245	52·5
274S	13·0	249	71·0	241	27·6	254	22·0
278	21·0	258S	18·0	247	26·8	261	22·5
285S	44·0	266	20·0	251	26·0	272S	32·0
289	88·0	271	21·0	260S	32·0	283	63·5
292	59·0	276	24·0	263S	35·6	294	112·5
297	127·0	291	27·0	272	51·2	301S	31·5
301	270·0	299S	33·0	282S	42·8	317	45·5
308S	32·0	302	37·0	291	58·4	331	78·5
312S	22·0	315	33·0	303	78·4	381	4·4
316	19·0	343S	9·8	324	6·4	402	11·0
323	24·0	359	15·2	339	12·8	427	22·8
328	7·0	375	13·3	354	22·4	455	30·6
332	18·0	383	10·7	370	22·8		
338	65·0	403	5·8	372	23·6		
344	12·5	408	5·9	383	2·4		
355c	1·1	420	4·7	392	1·2		
362c	0·52	427	4·5				
365Sc	0·51	432	4·1				
378Sc	0·42	447	2·0				
381c	0·56	453	1·6				
387c	0·66	461	1·3				
394c	0·22						
397Sc	0·22						
402c	0·33						
409c	0·41						
419c	0·11						
427c	0·14						

TABLE 1. ULTRAVIOLET ABSORPTION SPECTRA OF POLYNUCLEAR HYDROCARBONS IN PENTANE (*continued*)

Benzo[*g,h,i*] perylene		Naphtho[1,2-*b*] thianaphthene		Dinaphtho [2,1,1′,2′]furan		Benzo[*b*]naphtho [2,1-*d*]furan	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
~222	37·8	238S	37·0	238	25·0	237S	31·0
230S	15·6	243	48·0	250	29·0	241	33·0
245S	14·2	251	53·0	257	31·0	250	45·0
253	18·4	256S	29·0	287	8·0	255S	40·0
269	25·6	265	25·0	298	13·0	258	104·0
276	27·6	274	40·0	323	9·0	274S	11·5
287	45·2	292	13·4	336	22·0	280S	13·5
299	62·0	303	16·0	347S	15·0	286S	17·7
312	5·6	315	5·5	352	39·0	288	17·9
324	5·0	331	2·4	390c	0·97	293	17·9
329	7·6	336	1·2	412c	2·14	298	20·0
344	10·6	340	0·9	439c	2·71	305S	10·6
361	22·6	348	3·2			310S	6·0
377S	21·0					316	2·6
382	28·2					324	5·4
390	3·0					331	2·9
394	1·6					339	8·5
405	0·42						

Benzo[*b*]naphtho [2,3-*d*]furan		Benzo[*k,l*] xanthene	
λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
239	34·0	~231	25·2
251	55·0	246	18·6
259	88·0	250	18·8
272	16·0	258S	12·3
277S	4·8	272	3·5
283	5·3	282	4·0
292	5·6	290	4·5
306	13·2	303	3·9
318	21·0	320S	3·1
333	8·0	337S	5·6
350	4·6	350	8·9
		364	11·2
		378S	6·3
		384	8·4

S = Shoulder.
a = Weak bands in pentane—more concentrated solution impossible.
b = $\epsilon \times 10^{-3}$ values taken from $CHCl_3$ solution of compound.
c = λmax. and $\epsilon \times 10^{-3}$ values taken from $CHCl_3$ solution of compound.

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approximately the same in both spectra. The most intense peak in the activation spectrum will give the most intense fluorescence spectrum. At the most intense activating wavelength, 381 mμ, the band at 403 mμ in the fluorescence spectrum of a 10^{-5}M solution of benzo[*a*]pyrene has a relative intensity of 19. At the less intense

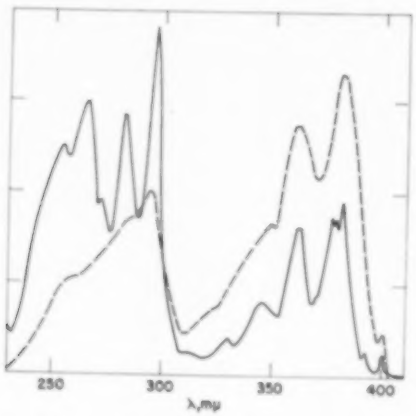

FIG. 1. Benzo[*a*]pyrene in pentane. ——— absorption spectrum; - - - - - activation spectrum at a fluorescent wavelength of 403 mμ.

activating wavelengths of 361 and 294 mμ, the fluorescence band at 403 mμ has intensities of 17 and 9, respectively. The other bands in the fluorescence spectrum at 427 and 454 mμ decrease proportionally. When the fluorescence monochromator is set at a wavelength maximum, an activation spectrum can then be obtained on the instrument. The most intense peak in the fluorescence spectrum will give the most intense activation spectrum. For example, with the fluorescence monochromator set at wavelengths 403, 427 and 454 mμ, the 381 mμ band of the activation spectrum of a 10^{-5}M benzo[*a*]pyrene solution will have relative intensities of 20, 14 and 4, respectively. The other bands in the activation spectrum at 361 and 294 mμ decrease proportionally. This type of information is of value in the analysis of mixtures, for there may be great interference at the strongest activating wavelength and relatively little at some weaker activating wavelength. *In many instances it is possible to obtain the pure fluorescence spectrum of an aromatic hydrocarbon in a mixture by determining the fluorescence spectrum of the mixture at an appropriate activating wavelength maximum of the aromatic hydrocarbon.* The value of this approach in the analysis of fluorescent compounds is described in detail after such factors as the sensitivity, fluorescence intensity and concentration effect are evaluated.

An interesting facet of fluorescence analysis is the sensitivity at which a hydrocarbon can be detected. Our definition of sensitivity is fairly rigid—it is the lowest concentration of a hydrocarbon in solution at which a definite unchanged characteristic fluorescence spectrum is obtained. For example, with slit arrangement No. 3 (where the narrowest slit widths are 1/16 in.), 0·001 μg of benzo[*a*]pyrene can be detected in 1 ml of pentane, while with slit arrangement No. 2, 0·003 μg can be detected. With slit arrangement No. 3, 0·0003 μg of anthanthrene can be readily detected. Essentially this means that 0·3 part per billion of this hydrocarbon can be detected in pentane.

For most of the other hydrocarbons discussed in this paper the sensitivity is in the order of milligamma per milliliter or parts per billion in pentane.

Related to sensitivity is the fluorescence intensity of a compound as compared to some standard. GREENGARD (1958) has suggested the probable utility of a coefficient of fluorescence which would relate the concentrations of compounds to their fluorescence intensity under defined conditions. Such values could prove useful in analytical work. For dilute solutions (where the concentration effect is negligible) the fluorescence intensity of a compound (F_x) is related to the concentration (C_x) as follows:

$$F_x = K_x C_x . \tag{1}$$

If the reference standard is a solution containing 1 μg of quinine per 1 ml of 0·1 N aqueous sulfuric acid, then

$$F_s = K_s C_s \tag{2}$$

where F_s is the fluorescence intensity of the strongest fluorescence band obtained at the most intense activating wavelength of quinine. In this case the activating wavelength is 350 mμ while the fluorescence intensity is measured at 450 mμ.

Dividing equation (1) by equation (2) yields:

$$\frac{F_x}{F_s} = \frac{K_x C_x}{K_s C_s}, \tag{3}$$

whence

$$\frac{K_x}{K_s} = \frac{F_x C_s}{F_s C_x}. \tag{4}$$

When $C_s = 1 \mu g/ml$,

then

$$K_Q = \frac{K_x}{K_s} = \frac{F_x}{F_s C_x} \tag{5}$$

where C_x is now the concentration of compound in micrograms per milliliter. Thus, at sufficiently low concentrations where Beer's Law is observed, K_Q is the relative fluorescence intensity of a compound compared to quinine. The reciprocal of this constant is the concentration of a compound, in μg/ml, that will give the same fluorescence intensity as 1 μg/ml of quinine in 0·1 N sulfuric acid. Admittedly, the K_Q values are arbitrary constants, but they have proven to be of value.

The K_Q values of various hydrocarbons are compared in Table 2. The comparative fluorescence intensities of some 330 fluorescent compounds have been reported (FURST *et al.*, 1957). *p*-Terphenyl was found to be the most intensely fluorescent. However, Table 2 lists eight hydrocarbons which are at least as intense as *p*-terphenyl.

An extremely important factor in fluorescence analysis is the concentration effect. This is a physical phenomenon, caused mainly by the dissipation of absorbed light energy in a molecule in the excited state by collision with another molecule, resulting in a decreased K_Q value. The more concentrated the solution, the more collisions take place, and the fewer molecules are left which can emit their quanta of light. If the compound being analyzed is present in too large a concentration, its K_Q value will decrease *and in more concentrated solutions its fluorescence spectral envelope will change drastically*. This phenomenon is shown for a solution of benzo[*a*]pyrene in dimethylformamide (Fig. 2). The same phenomenon takes place in pentane, although the effect is not as drastic.

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TABLE 2. COMPARISON OF FLUORESCENCE INTENSITIES OF POLYNUCLEAR HYDROCARBONS IN PENTANE

Compound	Wavelength maxima		K_Q
	Activation	Fluorescence	
Quinine			1·0
Anthanthrene	420	430	45
Naphtho[2,3-*a*]pyrene	457	458	~33
Perylene	430	438	32
Dibenzo[*b*,*k*]chrysene	308	428	17[a]
7-Methyldibenzo[*a*,*h*]pyrene	460	467	13[a]
Benzo[*k*]fluoranthene	302	400	13
Benzo[*a*]pyrene	381	403	6
1,4-Diphenylbutadiene	328	370	6
p-Terphenyl	284	338	6
Benzo[*k*,*l*]xanthene	363	418	5
11H-Benzo[*a*]fluorene	317	340	4
11H-Benzo[*b*]fluorene	312	340	4
7H-Benzo[*c*]fluorene	334	337	4
Benzo[*b*]naphtho[2,3-*d*]furan	320	350	4
Anthracene	350	398	3
Benzo[*b*]chrysene	283	398	2
9-Methylanthracene	382	410	2
3-Methylcholanthrene	297	392	2
Benzo[*b*]fluoranthene	300	428	2
Dibenzo[*a*,*e*]pyrene	370	401	2
Tribenzo[*a*,*e*,*i*]pyrene	384	448	2
Dibenz[*a*,*h*]anthracene	292	394	1
Fluorene	300	321	1
Benz[*a*]anthracene	284	382	0·9
7,12-Dimethylbenz[*a*]anthracene	293	427	0·8
Fluoranthene	354	464	0·8
Dibenz[*a*,*j*]anthracene	300	410	0·7
Dibenz[*a*,*c*]anthracene	280	381	0·7
Picene	281	398	0·7
4-Methylpyrene	338	386	0·7
o-Phenylenepyrene	360	506	0·6
1-Methylpyrene	336	394	0·6
Chrysene	264	381	0·6
Coronene	337	450	0·6
Pyrene	330	382	0·5
3-Methylphenanthrene	292	368	0·5
Benzo[*e*]pyrene	329	389	0·4
Benzo[*g*,*h*,*i*]perylene	280	419	0·4
Acenaphthene	291	341	0·4
Phenanthrene	252	362	0·2
2-Methylphenanthrene	257	357	0·2
4-*Cyclo*penta[*d*,*e*,*f*]phenanthrene	294	362	0·2
Triphenylene	287	357	0·1
5,12-Dihydronaphthacene	282	340	0·1

[a] In chloroform.

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The concentration effect can adversely affect the analysis of a hydrocarbon in a mixture. Excess hydrocarbon molecules of any type will radically decrease this fluorescence intensity. For example, the analysis for benzo[*e*]pyrene in a mixture

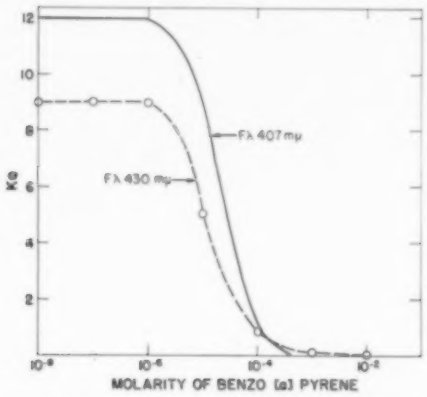

FIG. 2. The effect of increasing concentration of benzo[*a*]pyrene in dimethylformamide on the fluorescence intensity. Activating wavelength 381 mμ.

containing increasing amounts of benzo[*a*]pyrene is shown in Fig. 3. The K_Q value is decreased, and the contour of the fluorescence spectrum is drastically altered. For the fluorometric analysis of a compound in a mixture, it is recommended that the concentration of the mixture be kept constant and low.

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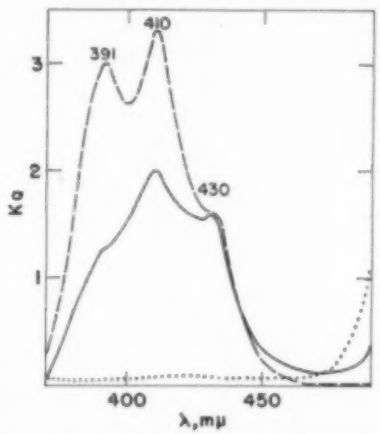


FIG. 3. Concentration effect on the determination of benzo[*e*]pyrene in the presence of benzo[*a*]pyrene. All solutions in sulfuric acid 10^{-6}M in benzo[*e*]pyrene. Activating wavelength 362 mμ. - - - - - 10^{-5}M or lower concentrations of benzo[*a*]pyrene; ——— 10^{-4} benzo[*a*]pyrene; . . . . 10^{-3}M benzo[*a*]pyrene.

The activation and fluorescence spectral data in Tables 3 and 4 are invaluable in the analysis for an individual polynuclear hydrocarbon in a mixture of aromatic hydrocarbons. For example, it is apparent that, in a mixture of benzo[*a*]pyrene and benzo[*e*]pyrene, both hydrocarbons can be readily determined either in pentane or in

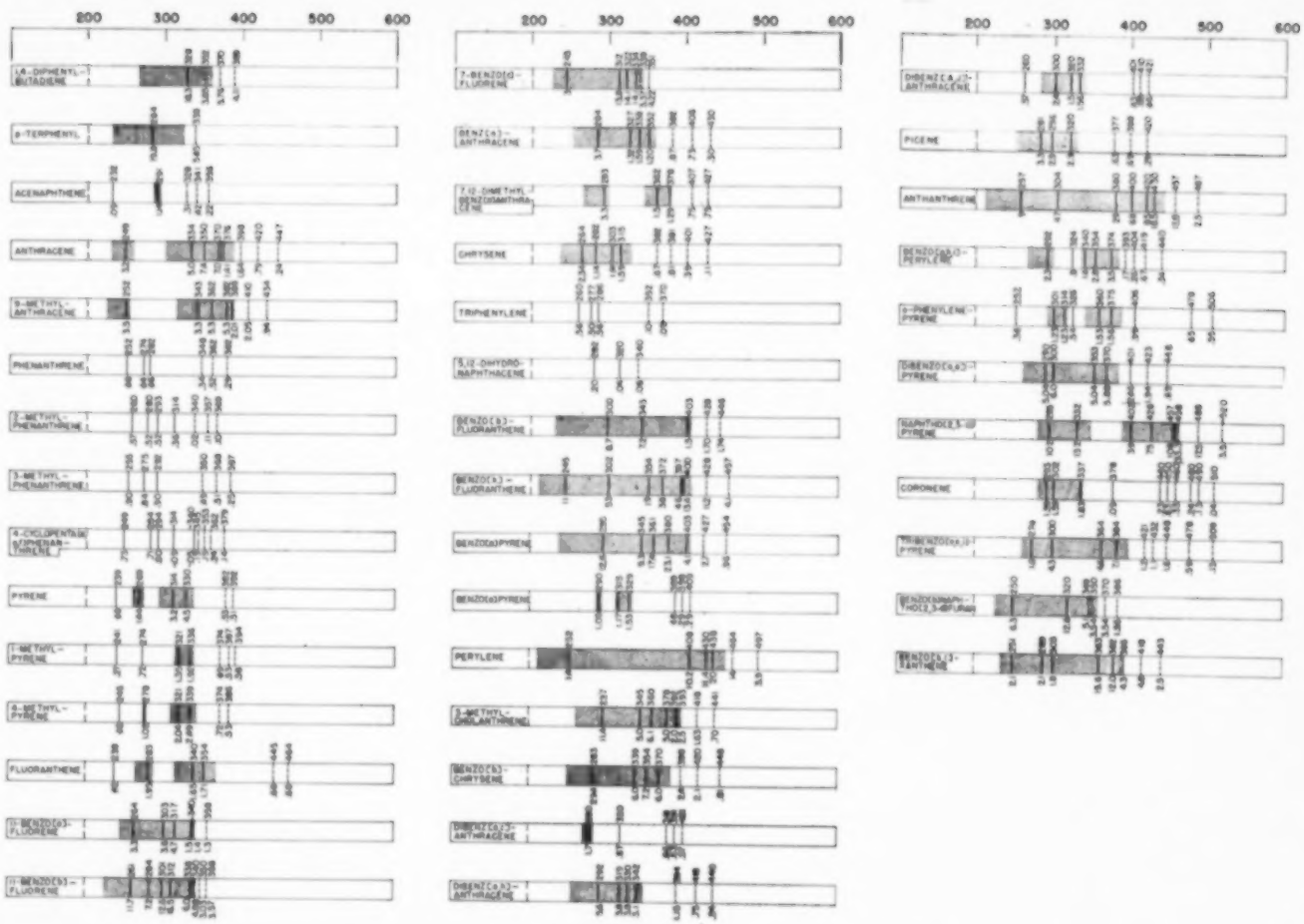
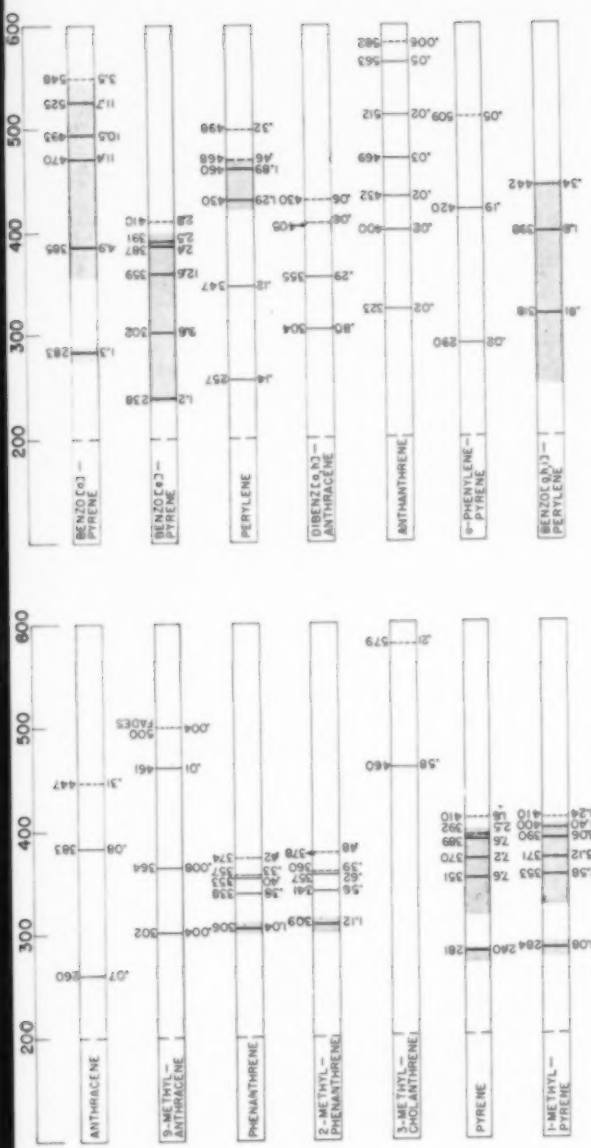


TABLE 3. ACTIVATION AND FLUORESCENCE SPECTRAL DATA IN PENTANE

Activation spectral maxima are denoted by a solid line. Values above this line are activation wavelength maxima; values below this line are MT values, e.g. microphotometer meter reading times the meter multiplier reading. Fluorescence spectral maxima are denoted by a dashed line. Values above this line are fluorescence wavelength maxima obtained at the strongest activation wavelength; values below the line are *Ko* values



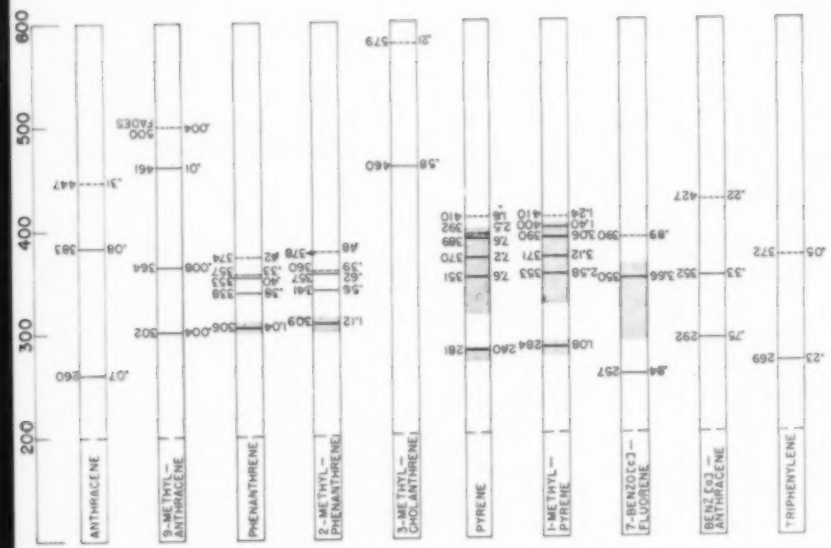


TABLE 4. ACTIVATION AND FLUORESCENCE SPECTRAL DATA IN SULFURIC ACID

Activation spectral maxima are denoted by a solid line. Values above this line are activation wavelength maxima; values below this line are MT values, e.g. microphotometer meter reading times the meter multiplier reading. Fluorescence spectral maxima are denoted by a dashed line. Values above this line are fluorescence wavelength maxima obtained at the strongest activation wavelength; values below the line are K_Q values. All activation spectral values above MT = 1 are shaded. All solutions are 10^{-5}M.

sulfuric acid. In pentane, benzo[*e*]pyrene will be determined at an activating wavelength of 315 mμ while benzo[*a*]pyrene will be determined near 380 mμ. In sulfuric acid, benzo[*e*]pyrene can be determined at activating wavelength 302 or 359 mμ (see Fig. 3) while benzo[*a*]pyrene can be determined at 470, 493 or 525 mμ. As benzo[*a*]pyrene and benzo[*e*]pyrene are difficult to separate chromatographically, this method of analysis should prove to be of value.

Benzo[*a*]pyrene and perylene are usually found together and are hard to separate chromatographically. However, from Table 3 it is apparent that benzo[*a*]pyrene can be determined at activating wavelength 295 mμ while perylene can be determined at 430 mμ. Fig. 4 clearly demonstrates this prediction. In using these tables, other

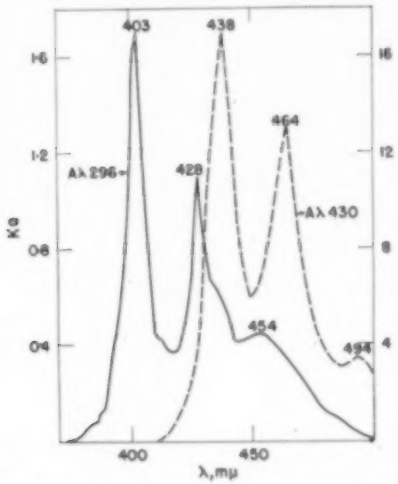


FIG. 4. Mixture of benzo[*a*]pyrene (10^{-5}M) and perylene (10^{-5}M) in pentane.

factors such as the relative intensities of the activating wavelength bands, the K_Q values and the concentration effect must be considered.

In Tables 3 and 4, values of MT (photomultiplier microphotometer reading × meter multiplier reading) of 1·0 have been arbitrarily chosen as activation cutoff values. The ideal situation is to analyze for a compound at a fairly prominent activation wavelength maximum, at which wavelength the other compounds in the mixture are only weakly activated. The analytical specificity of this approach is truly remarkable in some cases. For example, 0·03 μg of perylene or anthanthrene can be readily detected in mixture *A* containing 30 μg of hydrocarbons per milliliter of pentane. The pure fluorescence spectrum of the compound is obtained with very little contribution from the other twenty-five hydrocarbons (Fig. 5). The extraordinary specificity and sensitivity of this method is shown by the fact that 1 ml of a pentane solution of 5 μg of mixture *B* containing 0·05 μg of naphtho[2,3-*a*]pyrene gave the pure fluorescence spectrum of naphtho[2,3-*a*]pyrene when activated at 450 mμ. In spite of the presence of many related hydrocarbons, analysis of the mixture for naphtho[2,3-*a*]pyrene gave a value of 0·04 μg/ml.

For the last 30 years the analysis for benzo[*a*]pyrene in mixtures consisted of chromatography followed by ultraviolet or fluorescence spectral analysis of the fractions.

The fluorometric method depended on obtaining the fluorescence spectrum of an aromatic mixture in some inert solvent at an arbitrary activating wavelength or range of wavelengths, and then by comparison of this spectrum with a benzo[*a*]pyrene spectrum crudely estimating the amount present. In this method the background fluorescence is high. As benzo[*k*]fluoranthene has a fluorescence spectrum very

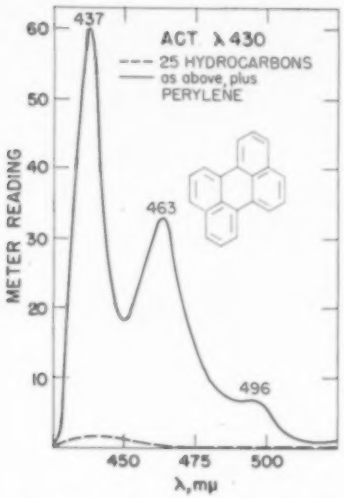


FIG. 5. Fluorescence spectra at activating wavelength 430 mμ in pentane. - - - - - mixture *A* (see Experimental)—each hydrocarbon 10^{-7}M; ——— same solution plus 5×10^{-8}M perylene.

similar to that of benzo[*a*]pyrene while benzo[*b*]fluoranthene, anthanthrene and anthracene have two to three peaks which coincide with those of benzo[*a*]pyrene, analytical results could only be expected to be crude approximations. The ultraviolet method depends on analyzing at the 382 mμ peak of benzo[*a*]pyrene. However, many hydrocarbons have bands within ± 2 mμ of the 382 mμ band, e.g. 9-methylanthracene, benz[*a*]anthracene, 7,12-dimethylbenz[*a*]anthracene, benzo[*b*]carbazole, dibenzo[*b,g*]phenanthrene, benzo[*k*]fluoranthene, perylene, benzo[*b*]chrysene, benzo[*c*]chrysene, indeno[1,2,3-*d*]pyrene, benzo[*b*]picene, anthanthrene, naphtho [2,3-*a*]pyrene and benzo[*g,h,i*]perylene. So here again, unless all the compounds that have peaks near 382 mμ are identified in the mixture, analysis at this band is essentially an estimation.

A simple, specific and sensitive method for the detection of benzo[*a*]pyrene in mixtures is not available in the literature. In this respect the new method shows promise. The activation and fluorescence spectra of benzo[*a*]pyrene in sulfuric acid (Fig. 6) are an integral part of this procedure. The stability of a benzo[*a*]pyrene solution in sulfuric acid under ordinary room conditions and under illumination is depicted in Fig. 7. Standing at room temperature near a window, the benzo[*a*]pyrene solution is stable for 30 min; under steady illumination the intensity decreases fairly rapidly. The specificity and the sensitivity of the method are of a high order. As can be seen from Table 4, benzo[*a*]pyrene is one of the few hydrocarbons that has an activating wavelength at 520 mμ in sulfuric acid. Anthanthrene does have an activating peak at 512 mμ, but it has one-fiftieth of the intensity of the benzo[*a*]pyrene

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peak. When the fluorescence spectra in sulfuric acid of the different hydrocarbons are compared, benzo[*a*]pyrene is the only one that has a band near 545 mμ. Anthanthrene does have a band at 582 mμ, but the benzo[*a*]pyrene band is approximately 600 times as intense. The other activating wavelengths of benzo[*a*]pyrene can be used in the analysis depending upon the kind of other compounds present in the mixture.

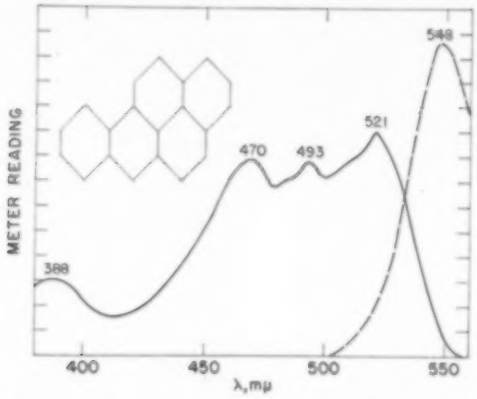

FIG. 6. Benzo[*a*]pyrene 10^{-6}M in sulfuric acid. ——— activation spectrum at fluorescent wavelength 545 mμ; - - - - - fluorescence spectrum at activating wavelength 520 mμ.

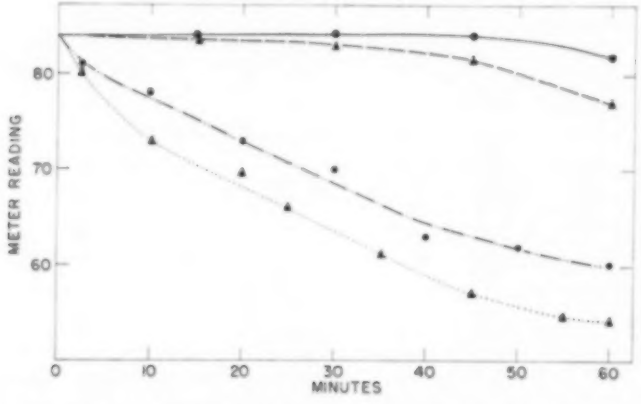

FIG. 7. Effect of time on the intensity of the fluorescence wavelength maximum at 545 mμ of a 2×10^{-6}M solution of benzo[*a*]pyrene in concentrated sulfuric acid. ——— unilluminated solutions, activating λ520 mμ; —— . . .—— steady illumination at 520 mμ; - - - - - unilluminated solutions, activating λ470 mμ; . . . . steady illumination at 470 mμ.

The extraordinary specificity of the new method is shown by the ready detection of benzo[a]*pyrene in a mixture containing some fifty polynuclear aromatic hydrocarbons* (Fig. 8). Actually 0·04 μg of benzo[*a*]pyrene can be detected in 1 ml of the sulfuric acid solution containing 50μg of mixture *B*.

Detection of benzo[a]*pyrene in a mixture*

For the unequivocal identification of benzo[*a*]pyrene in a mixture the following procedure is recommended.

(a) The mixture is extracted with benzene for 4 hr in a Soxhlet extraction apparatus.
(b) The benzene is evaporated under a vacuum at room temperature.
(c) The residue and container are weighed; then the residue is dissolved in a definite volume of chloroform.

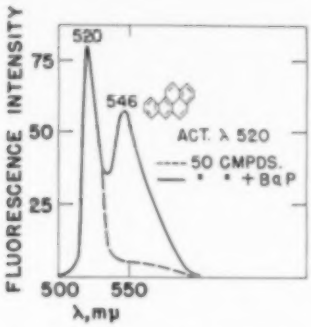

FIG. 8. Fluorescence spectra at activating wavelength 520 mμ in sulfuric acid. ----- mixture *B* (see Experimental)—each hydrocarbon 10^{-6}M; ——— same solution plus 5×10^{-7} benzo[*a*]pyrene.

(d) The container is reweighed; the weight of residue in the chloroform is calculated.
(e) An aliquot of this solution is added to a test tube. The chloroform is evaporated at room temperature.
(f) Concentrated sulfuric acid is added to the residue to make the final concentration 50 μg of residue per 1 ml of sulfuric acid.
(g) The activation spectrum of benzo[*a*]pyrene is obtained in the spectrophotofluorometer at a fluorescence wavelength of 545 mμ (Fig. 6) if 0·1 per cent of the hydrocarbon is present in the organic sample.
(h) At the activating wavelengths of 470 and 520 mμ, a fluorescence wavelength maximum near 540–550 mμ is obtained if 1 per cent benzo[*a*]pyrene is present in the organic fraction. For lower concentrations of benzo[*a*]pyrene, the fluorescence wavelength maximum obtained at activating wavelengths of 470 and 520 mμ is below 540 mμ and above 550 mμ, respectively.

For the definite identification of benzo[*a*]pyrene in a mixture the criteria in (g) and (h) must be fulfilled.

APPLICATIONS

The low intensity long wavelength bands found in the visible spectrum of a polynuclear hydrocarbon are sometimes questionable. The issue then is whether these bands are due to the hydrocarbon or to an impurity. Usually the impurity is another polynuclear hydrocarbon. A pure hydrocarbon should give a closely similar fluorescence spectrum at all activating wavelengths. If a different fluorescence spectrum is obtained at the low intensity long wavelength visible band, then this band is due to an impurity. Clues to the identity of the impurity can then be obtained by comparing the activation and fluorescence spectra of the impurity with standards.

Use has been made of this phenomenon to detect and determine fluorescent impurities in hydrocarbon standards. Several commercial samples of benzo[*e*]pyrene

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were analyzed for benzo[*a*]pyrene and perylene by the ultraviolet visible and fluorescence procedures. The identification of perylene was based on

(a) the presence of the 406, 428 and 434 bands in the visible absorption spectrum in pentane,
(b) the presence of the 385, 408 and 430 bands in the activation spectrum, and
(c) the presence of the 438, 464 and 497 bands in the fluorescence spectrum.

The identification of benzo[*a*]pyrene was based on

(a) the presence of the 377, 379 and 382 absorption peaks in pentane,
(b) the presence of the 403, 427 and 454 fluorescence peaks in pentane, and
(c) the presence of the 545–548 mμ fluorescence peak in sulfuric acid.

A sample of benzo[*e*]pyrene gave 0·10 per cent and 0·12 per cent perylene by the fluorescence and visible spectral methods, respectively. Benzo[*a*]pyrene could not be found. A sample of benzo[*a*]pyrene obtained from coal tar gave 2·5 per cent and 2·4 per cent perylene by the fluorescence and visible spectral methods, respectively. This same sample gave 3·0, 2·9 and 2·8 per cent benzo[*a*]pyrene by the visible, fluorescence (pentane) and fluorescence (sulfuric acid) methods, respectively.

It is necessary to stress that the fluorescence methods reinforce the ultraviolet-visible analytical procedures, since with these methods the identification of many hydrocarbons can be made with certainty and the determination of some of the hydrocarbons can be considerably simplified.

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SYMPOSIUM ON POLYCYCLIC HYDROCARBONS

THE DETECTION AND DETERMINATION OF POLYNUCLEAR HYDROCARBONS IN URBAN AIRBORNE PARTICULATES—I

THE BENZOPYRENE FRACTION*

E. SAWICKI, W. ELBERT, T. W. STANLEY, T. R. HAUSER and F. T. FOX
Air Pollution Engineering Research,
Robert A. Taft Sanitary Engineering Center,
Public Health Service,
U.S. Department of Health, Education, and Welfare
Cincinnati 26, Ohio
(*Received* 23 *July* 1959)

Abstract—A new simple procedure for the determination of benzo[*a*]pyrene in complex mixtures is introduced. A comparison of the concentration of benzo[*a*]pyrene in the air of nine cities for the month of November, 1958, is given. Evidence is presented for the identification of each hydrocarbon found in the benzopyrene fraction. The relative concentration of benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*k*]fluoranthene and perylene in the nine cities is approximately constant.

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THE effect on human beings of carcinogens present in the environment has been difficult to evaluate due to the lack of simple, specific, sensitive methods for the detection and determination of these chemicals. Many polynuclear compounds are known to be carcinogenic (HARTWELL, 1951; HADDOW and KON, 1947). Of these compounds benzo[*a*]pyrene (hereafter named B*a*P) has been investigated most thoroughly. It has been found in cigarette smoke, tars, in various combustion processes, and in the air. All analytical work in this field has been bedeviled by the lack of a simple, sensitive procedure for the determination of B*a*P. In this paper such a method is introduced.

As further knowledge is obtained about the number and complexity of aromatic compounds present in air particulates, it is apparent that identification of a compound by the presence of one or two ultraviolet bands in a chromatographed fraction is by no means unequivocal.

A simple, analytical methodology for the characterization of polynuclear hydrocarbons in chromatographed air particulate fractions is necessary as a guideline for further study and development in this field. An attempt has therefore been made to itemize the evidence for the identification of polynuclear hydrocarbons in the chromatographed fractions.

EQUIPMENT AND MATERIALS

The absorption spectra were determined with a Cary recording spectrophotometer Model II. Activation and fluorescence spectra were obtained with an Aminco–Bowman spectrophotofluorometer. A Technicon time–flow fraction collector was

* Presented before the American Chemical Society, Air Pollution Symposium, 136th National Meeting, Atlantic City, N.J., September 1959.

used in the column chromatographic work. The glass column used for the chromatographic work was $\frac{1}{2}$ in. in diameter and 15 in. long with a drain at one end and a ground glass joint at the other. This joint permits connection to a liquid reservoir without contamination. Thermo-Vac ovens (Schaar and Company, Chicago 34, Ill.) were used for evaporation of pentane solutions at room temperature in the dark under a vacuum. Pentane was distilled before use.

For the chromatographic work, Merck acid-washed aluminum oxide was washed with ether, dried, and heated in an oven at 130°C for 30 hr. Then 1·4 per cent water was stirred into the alumina. The mixture was then allowed to equilibrate for at least 24 hr in a stoppered bottle. The alumina then contained 13·4 per cent water (as determined by weighing a sample and then heating to red-hot heat for 10 min, cooling in a desiccator, and reweighing). This alumina is excellent for separating the benzopyrene fraction. By the benzopyrene fraction is meant the chromatographic cut which contains all the benzo[*a*]pyrene and benzo[*e*]pyrene and any other compounds which have essentially the same R_F value on the column. When the percentage of water in the alumina is gradually decreased, the benzopyrene fraction is more slowly eluted and more cleanly separated from the benzoperylene fraction. The ideal situation is to adjust the water to have the peak amount of B*a*P come out in a tube at around 150–250 ml of eluent.

Davison silica gel, mesh size 100–200, was washed with ether, dried and heated at 130° for 1 hr and then stored in a glass-stoppered bottle.

Benzene extracts of air particulate samples from nine American cities were obtained by the National Air Sampling Network of the U.S. Public Health Service. Aromatic fractions (TABOR *et al.*, 1958) of these air particulate samples are being routinely separated by the National Air Sampling Network for a carcinogenicity study.

CHROMATOGRAPHIC PROCEDURE

The following procedure is essentially a modification of the method of FALK and STEINER (1952). One gram of alumina was added to a small volume of chloroform solution containing 50–150 mg of the benzene-soluble fraction or 10–50 mg of the aromatic fraction. The chloroform was evaporated. This mixture was then added to the column which consisted of a lower layer of 9 g of alumina and an upper layer of 0·5 g silica gel. The column was then eluted with 100 ml of pentane containing 6 per cent ether, followed by 250 ml of pentane containing 8 per cent ether. During this operation the column was protected from the light. Fractions of approximately 10–20 ml were collected. They were then evaporated in a vacuum oven at room temperature in the dark.

CHARACTERIZATION OF THE HYDROCARBONS IN THE BENZOPYRENE FRACTION

The chromatographic procedure described is ideal for the isolation of the benzopyrene fractions. A typical fraction of this type is shown in Fig. 1. A similar spectral curve has been obtained for every city so far studied. It would thus appear that the proportion of the major hydrocarbons in the benzopyrene fractions is fairly constant from city to city. The approximate proportions of B*a*P, benzo[*e*]pyrene, benzo[*k*]-

fluoranthene and perylene are 8:5:3:1. These results merit further investigation. The presence of a sharp peak at 331 mμ in Fig. 2 indicates the presence of benzo[*e*]-pyrene. In fact, comparison of part of the ultraviolet absorption spectrum of a benzopyrene fraction with a comparable spectrum of benzo[*e*]pyrene even more

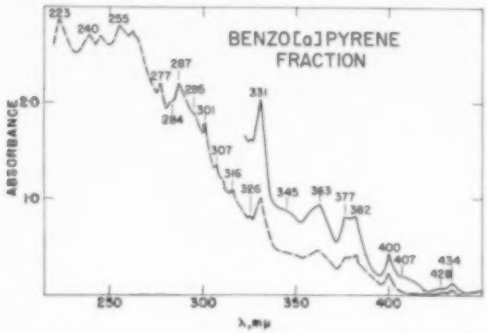

FIG. 1. Ultraviolet absorption spectra of the benzopyrene fraction in pentane.

strongly suggests the presence of the latter hydrocarbon (Fig. 2). The clear-cut characterization of benzo[*e*]pyrene in the benzopyrene fraction is evident from the fluorometric data in Fig. 3. The fluorescence data in sulfuric acid are especially convincing. In spite of the complexity of this benzopyrene fraction, a pure fluores-

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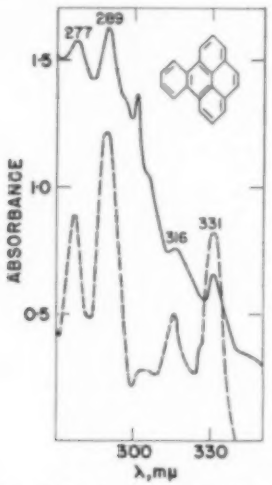

FIG. 2. Ultraviolet absorption spectra in pentane.
——— benzopyrene fraction; - - - - pure benzo[*e*]pyrene.

cence spectrum of benzo[*e*]pyrene in sulfuric acid is obtained. The use of appropriate activation and fluorescence wavelength maxima to detect hydrocarbons in extremely complicated mixtures has been discussed in a previous paper (SAWICKI *et al.*, 1960). Evidence for the characterization of benzo[*e*]pyrene is summarized in Table 1.

The bands at 428 and 434 mμ and the shoulder at 407 mμ in the visible spectrum of the benzopyrene fraction (Fig. 1) are attributed to perylene. A solution of the benzo-

pyrene fraction in pentane gave a fluorescence spectrum identical to that of perylene (Fig. 4).

Simple proof for the characterization of benzo[*k*]fluoranthene in the benzopyrene fraction is difficult to obtain. Activation spectra of the benzopyrene fraction obtained

TABLE 1. EVIDENCE FOR PRESENCE OF BENZO[*e*]PYRENE IN BENZOPYRENE FRACTION

	Solvent	λmax, mμ	
		Fraction	Benzo[*e*]pyrene
Ultraviolet spectra	Pentane	287, 277, 316, 331	288, 277, 331, 316
Act. spectra, F. λ389	Pentane	329, 290s	329, 315, 290
F. spectra, Act. λ330	Pentane	388	388, 408, 398
F. spectra, Act. λ362	H_2SO_4	410, 391, 427s	410, 393, 430s

at fluorescence wavelengths 403, 428 and 457 mμ show the presence of an intense band at 400 mμ (apparently due to benzo[*k*]fluoranthene) and a somewhat less intense band at 380 mμ (due to B*a*P). The remainder of the bands are what would be expected from a mixture of these two hydrocarbons. Activation at 380 or 400 mμ gives a

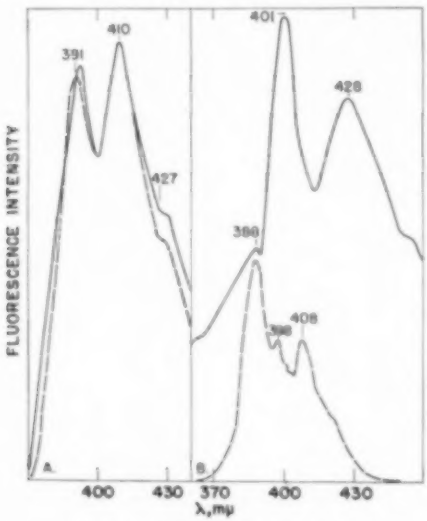

FIG. 3. Fluorescence spectra.

(A) In sulfuric acid at activating wavelength 362 mμ. ——— benzopyrene fraction; - - - - benzo[*e*]pyrene.

(B) In pentane at activating wavelength 330 mμ. ———benzopyrene fraction; - - - - benzo[*e*]pyrene.

fluorescence spectrum closely similar to that of B*a*P or benzo[*k*]fluoranthene. Activation at 400 mμ gives the more intense fluorescence spectrum. This fact indicates the presence of the more intensely fluorescent benzo[*k*]fluoranthene.

To check the characterization of these hydrocarbons, a synthetic mixture containing 250 γ B*a*P, 100 γ benzo[*k*]fluoranthene, 150 γ benzo[*e*]pyrene, and 50 γ of perylene was chromatographed by the standard procedure (using alumina containing 2·8 per cent

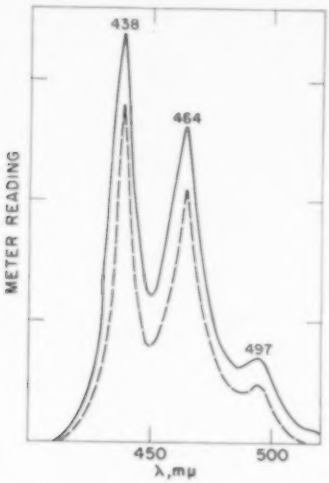

FIG. 4. Fluorescence spectra in pentane at activating wavelength 430 mμ. ——— benzopyrene fraction; - - - - perylene.

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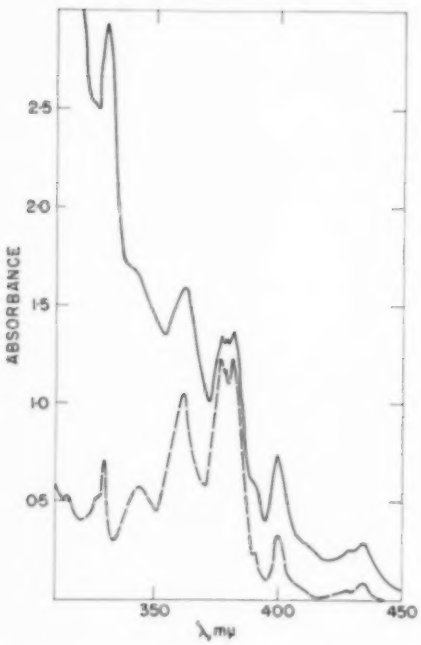

FIG. 5. Ultraviolet-visible absorption spectra in pentane. ——— benzopyrene fraction from air particulates; - - - - benzopyrene chromatographic fraction from synthetic mixture of 250 γ BaP, 100 γ benzo[*k*]fluoranthene, 150 γ benzo[*e*]pyrene and 50 γ of perylene.

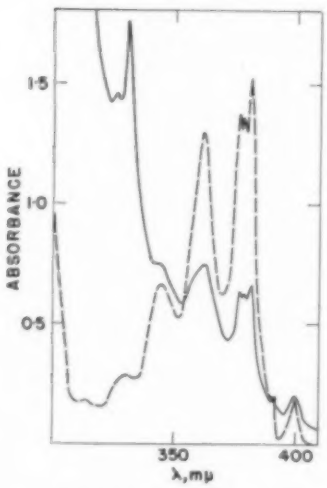

FIG. 6. Ultraviolet absorption spectra in pentane. ——— benzopyrene fraction; - - - - benzo[*a*]pyrene.

water). The entire mixture was found in two tubes. If allowances were made for the background absorption in the air sample, the absorption spectrum of the synthetic fraction was closely similar to the benzopyrene fraction as obtained from air particulates (Fig. 5).

Comparison of the ultraviolet spectra of the benzopyrene fraction and B*a*P (Fig. 6) indicates the presence of B*a*P in the fraction. This belief is confirmed by a visible

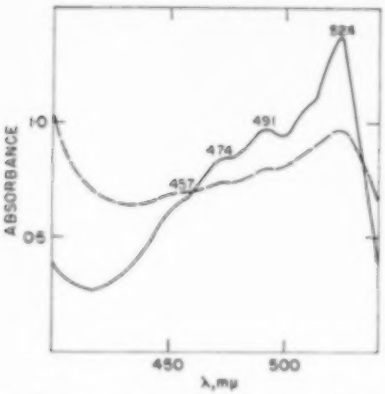

FIG. 7. Visible absorption spectra in trifluoroacetic acid–0·6 per cent sulfuric acid.
---- benzopyrene fraction;
——— benzo[*a*]pyrene.

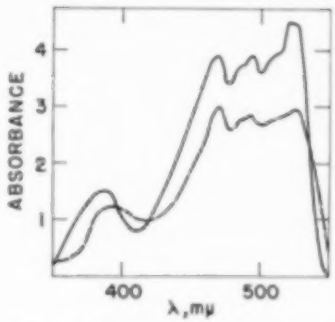

FIG. 8. Activation spectra in sulfuric acid at a fluorescence wavelength of 545 mμ.
---- benzopyrene fraction;
——— benzo[*a*]pyrene.

spectral comparison of the benzopyrene fraction and B*a*P in trifluoracetic acid–0·6 per cent sulfuric acid (Fig. 7). In this solvent most of the B*a*P forms a cation absorbing in the visible, while the other hydrocarbons are too weakly basic to form a cation and/or absorb only slightly in the visible. An activation spectral comparison of the fraction and B*a*P further substantiates the identification of B*a*P in the fraction (Fig. 8). The complete data on the characterization of benzo[*a*]pyrene are summarized in Table 2.

TABLE 2. EVIDENCE FOR PRESENCE OF BENZO[*a*]PYRENE IN BENZOPYRENE FRACTION

	Solvent	Common bands; λmax, mμ Benzo[*a*]pyrene and fraction
Ultraviolet spectra	Pentane	See Fig. 6
Vis. spectra	CF_3COOH–0·6% H_2SO_4	524, 491, 474s
Act. spectra, F. λ545	H_2SO_4	470, 485, 494, 510, 522
F. spectra, Act. λ381	Pentane	403, 428, 453
F. spectra, Act. λ470 or 520	H_2SO_4	545

DETERMINATION OF BENZO[*a*]PYRENE IN COMPLEX MIXTURES

Determination of BaP in the chromatographic fractions

The residue in each tube was dissolved in exactly 3 ml of pentane and the solution was then scanned from 210 to 500 mμ with a spectrophotometer. Since 24·8 μg of

B*a*P contained in a 3-ml cell of 1 cm width gives an absorbance of 1·00 at 382 mμ, the micrograms of benzo[*a*]pyrene in each fraction can be determined. The amounts of benzo[*k*]fluoranthene (analyzed at λ max 400 mμ) and perylene (analyzed at λ max 434 mμ) must be determined so that their contribution to the 382 mμ band can be subtracted. Similarly if any other hydrocarbons are present, their contribution must be subtracted. As a check, the base line method of COOPER (1954) was also used. At the most, the authors consider these methods good estimations.

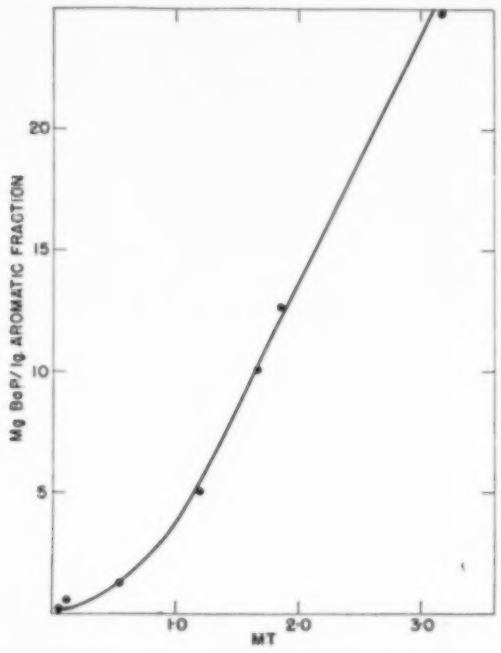

FIG. 9. MT (e.g. microphotometer meter reading multiplied by meter multiplier value) versus mg B*a*P in 1 g of aromatic fraction. Concentration of aromatic fraction is 50 μg/ml sulfuric acid. The standard solution consists of a 5×10^{-6}M concentration in sulfuric acid of each of the ~50 compounds as listed in the experimental section.

Determination of BaP in the aromatic fraction

(a) *The standard solution.* This mixture consists of the following compounds (each 5×10^{-6}M in pentane): benzene, toluene, xylene, durene, diphenylmethane mesitylene, biphenyl, *o*-terphenyl, *m*-terphenyl, *p*-terphenyl, *p*-quaterphenyl, phenyl ether, phenyl sulfide, naphthalene, fluorene, 2-methylfluorene, 2-ethylfluorene, dibenzofuran, dibenzothiophene, 9,9′-difluorenyl, anthracene, 9-methylanthracene, phenanthrene, 2-methylphenanthrene, 3-methylphenanthrene, 9, 10-dimethylbenz[*a*]-anthracene, acenaphthene, fluoranthene, triphenylene, 4-*cyclo*penta[*d,e,f*]phenanthrene, 11H-benzo[*a*]fluorene, 11H-benzo[*b*]fluorene, 7H-benzo[*c*]fluorene, chrysene, pyrene, 1-methylpyrene, 4-methylpyrene, benz[*a*]anthracene, 3-methylcholanthrene, benzo[*e*]pyrene, dibenz[*a,h*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, picene, benzo[*c*]phenanthrene, benzo[*g,h,i*]perylene, perylene, anthanthrene, and coronene. The sulfuric acid solution was prepared by evaporating an appropriate

volume of the above solution and diluting to the mark in the appropriate volumetric flask. At the same time the concentration of B*a*P in the mixture is varied, while the total concentration of all the components is kept constant at 50 μg/ml (and 5×10^{-6}M for each component).

(b) *Procedure*. Using appropriate chloroform aliquots of the aromatic fraction of air particulate matter followed by evaporation and solution in sulfuric acid to a 50 μg/ml concentration, the concentration in milligrams of B*a*P per gram of aromatic fraction can be quickly ascertained in the following manner. With the spectrophotofluorometer set at a sensitivity of 50 and an activating wavelength of 520 mμ, the

Table 3. Comparison of some methods for the determination of B*a*P in the aromatic fraction of air particulates, November, 1958

City	mg B*a*P/1 g of aromatic fraction	
	S_1*	Q†
City *A*	0·15	<0·2
City *B*	0·64	0·70
City *C*	0·75	0·60‡
City *D*	0·87	0·80
City *E*	2·4	2·2
City *F*	3·5	5·5
City *G*	4·6	4·6
City *H*	5·9	6·4
City *I*	7·7	9·2

* Method involving chromatography followed by ultraviolet analysis at 382 mμ.
† Fluorescence method in sulfuric acid. Activating at 520 mμ and analysis at wavelength maximum near 545 mμ.
‡ Most of sample insoluble in sulfuric acid.

microphotometer reading is determined at the fluorescence wavelength maxima of approximately 545 mμ. This figure, multiplied by the meter multiplier reading, gives an MT value directly proportional to the B*a*P concentration (Fig. 9). A scatter peak at 520 mμ in the fluorescence spectrum is apparently caused by the presence of fine air bubbles in the solution after the residue is dissolved in the sulfuric acid. This scatter peak can be minimized by allowing the sulfuric acid solution to stand for 5–10 min. A solution of benzo[*a*]pyrene in sulfuric acid is stable for at least 30 min, although it is gradually decomposed if it is irradiated with a light of wavelength 470 or 520 mμ since its fluorescence intensity at 545 mμ decreases rapidly.

Discussion

In fluorometric analysis of a complex mixture, the total concentration of the mixture must be kept constant, so as to control the concentration effect. The standard curve in Fig. 9 was obtained with this premise in mind. The assumption is made here that the quenching effect is directly proportional to the number of molecules colliding with molecules of the fluorescent compound, and this latter number is proportional to the total concentration of the solution. On the basis of this assumption, the amount of B*a*P in 1 g of aromatic fraction for each of the nine cities has been determined. These amounts have been compared with the method involving chromatography followed by ultraviolet analysis at 382 mμ by the subtraction method (Table 3). Because of the many variables involved in a B*a*P determination (e.g. collection, chromatography,

absorbance by unknown compounds at the analysis peak, etc.), all known methods are, at best, good estimations. The new method has fewer variables, is much simpler and involves little time. Benzo[*g,h,i*]perylene, which can interfere drastically in the ultraviolet methods for the determination of B*a*P, and benzo[*k*]fluoranthene which seriously interferes with the usual fluorometric methods of analysis for B*a*P, have no unfavorable effect in the new procedure. Two disadvantages exist—one, that very low concentrations of B*a*P can be only crudely estimated, as in the Los Angeles aromatic fraction, and two, that instrumental reproducibility of the spectrophoto-

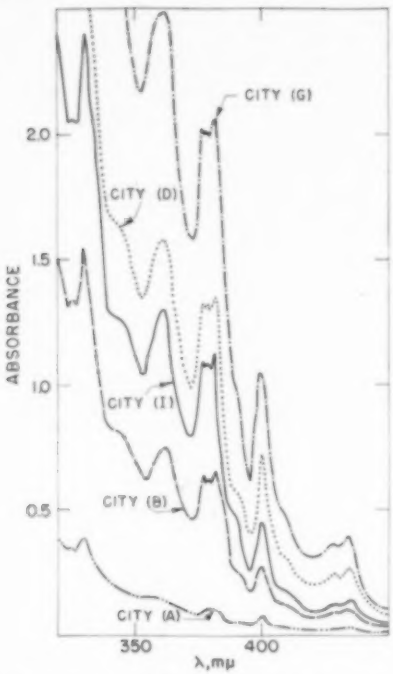

FIG. 10. Ultraviolet-visible absorption spectra in pentane of some benzopyrene chromatographic subfractions of the benzene-soluble fractions of air particulates from five cities. All particulate samples were collected in November 1958. Each benzene-soluble fraction weighed 150±15 mg. The chromatographic subfraction was in all cases the peak fraction for B*a*P.

fluorometer does not approach that of absorption spectrophotometers. However, the advantages of the new method outweigh the disadvantages. This procedure should be capable of greater accuracy with improvement in instrumentation.

The standard curve is best obtained from a fairly complex mixture of polynuclear hydrocarbons while varying the concentration of B*a*P. However, the standard curve can also be obtained by analyzing mixtures by the chromatographic–ultraviolet method and then by obtaining the fluorescence MT values of the samples. The application of this fluorometric procedure to more complicated mixtures is being investigated.

Following a close study of the spectra of chromatographic fractions from a large number of air particulate samples, we have reached the conclusion that an increase in the concentration of B*a*P denotes an increase in the concentration of many of the

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other well-known polynuclear hydrocarbons. Fig. 10 clearly demonstrates some of the evidence for this conclusion. The relative heights of the different bands in each curve are approximately constant. Assuming that (a) the concentration of most of the polynuclear compounds is roughly proportional to the concentration of B*a*P,and (b) among these compounds are the polynuclear carcinogens, then a measure of B*a*P is a relative measure of the total polynuclear carcinogens present in air particulates. On this basis we suggest the concentration of B*a*P in $\mu g/10^3 M^3$ value be called a " B*a*P index ". The index should prove of great value in studying the human chemical environment.

A study of the B*a*P content of nine American cities, with their various types of air pollution problems, has shown interesting results (Table 4). As these indices are

TABLE 4. BENZO[*a*]PYRENE CONCENTRATION FOR NINE AMERICAN CITIES, NOVEMBER, 1958

City	μg B*a*P/1 g particulate	μg B*a*P/1000 m^3 air
City *A*	5·1	1·9
City *B*	30·0	3·2
City *C*	32·0	2·9
City *E*	39·0	7·0
City *D*	54·0	7·6
City *I*	70·0	10·3
City *H*	98·0	14·4
City *F*	102·0	19·6
City *G*	106·0	29·9

values of pooled samples taken from several sites in each city, some areas in each city would be expected to have even higher values. The time of the year is also an extremely important variable in many areas of the country. This factor is being investigated.

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POLAROGRAPHIC PROPERTIES OF SMOG AEROSOLS

H. MAYRSOHN and P. P. MADER
Research Division,
Air Pollution Control District,
Los Angeles County, California
(*Received* 3 *November* 1959)

Abstract—Based upon observations that atmospheric aerosols collected on filter papers exhibited oxidant properties, it seemed reasonable to expect that these aerosols would be electro-reducible, hence capable of rapid and precise analysis with the polarograph and dropping mercury electrode. Under the described experimental polarographic conditions, atmospheric aerosols yielded a simple, stable and consistent voltage pattern consisting of not more than two half-wave potential values, regardless of the geographical source of the sample. One wave was identified as due to lead ions. The second wave which was always present in samples taken during smog episodes, was not definitely identified, but is apparently associated with $(NO)_x$ olefin reaction products.

It was found that the aerosols resulting from automobile exhaust yielded polarograms strikingly similar to atmospheric aerosols and that the resultant diffusion current was a function of the olefin content of the original fuel.

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INTRODUCTION

NUMEROUS analytical processes, both chemical and physical, have been applied in studies of airborne liquid and solid particles. While the analysis of inorganic particulate matter has been well developed using conventional techniques, the organic aerosol fraction of the atmosphere remains largely of unknown structure and identity.

Some information about the ether-soluble aerosol components has been published, demonstrating that during smog episodes relatively high concentrations of organic constituents were present ; infrared analyses of the atmospheric ether-soluble aerosol fractions, and of similarly collected and processed synthetic aerosols showed similar elemental composition and molecular structures (MADER *et al.*, 1952). Later investigations indicated clearly that automotive exhausts after irradiation could cause physiological effects similar to those produced by smog ; these exhausts contained aerosols that seemed to be related to those found in the atmosphere during smog conditions (CANN *et al.*, 1954 ; LARSON *et al.*, 1955 ; SCHUCK *et al.*, 1958). All of these studies required extensive and laborious analytical procedures. Exploratory studies were initiated, therefore, in an attempt to develop a rapid and precise analytical procedure that would yield informative data about some of the constituents in smog aerosols.

Based upon observations that atmospheric aerosols exhibited oxidant properties, it was postulated that these substances would be electro-reducible, and therefore susceptible to analysis by polarography.

MATERIALS AND METHODS

Atmospheric aerosol samples were collected with a Staplex high-volume sampler* fitted with a glass fiber filter web† ; the sampler was positioned about 6 ft above

* Staplex Corp., Brooklyn, N. Y. † Mine Safety Appliances Corp., Pittsburgh, Pa.

ground level, away from buildings and automobile traffic flow, and operated at the rate of 75 ft³/min. Most of the samples used in this study represented about 7500 ft³ of air. At the termination of a sampling interval, the filter web was cut into pieces about 1 in. square and macerated for about 1 hr in 35 ml of 1·0 M aqueous lithium chloride. The slurry was filtered through a sintered glass funnel, and the filtrate was transferred to an " H " type electrolysis cell. The pH was not adjusted (the range was 3·8–6·6) in order that the extracted aerosols would not be altered in any way. The cell containing the sample and external calomel electrode was immersed in a constant temperature water bath maintained at 25°C ±0·2°. In order to deoxygenate the sample, nitrogen that had been passed over copper turnings heated to 450°C and then through a water tower was bubbled through the sample for 15 min. A dropping mercury electrode was then immersed in the sample, and an atmosphere of nitrogen was maintained above the sample during analysis. Polarograms were obtained with a Sargent Model III Polarograph*, using the mercury electrode as the cathode in the range of 0·0 to −1·5 or −2·0 V, and the saturated calomel electrode as the anode.

Samples of atmospheres from other urban areas in the United States and from London, England, were obtained from the U.S. Public Health Service in the form of aerosol collections on glass fiber filter mats that had been used under the same sampling conditions as those existing at the Los Angeles laboratories.

Automotive exhaust aerosols were collected and analyzed polarographically by the same procedure as that used for the atmospheric samples. These synthetic aerosols were obtained by introducing exhaust vapors from either an idling International Harvester cylinder engine or a Fairbanks Morse 2-cylinder engine into an 11,000-l. Plexiglas chamber through a steel tube connecting the muffler to the chamber. The steel tube was constructed so that exhaust concentrations in the chamber could be varied by deflecting part of the exhaust stream. Purified air was continually admitted to the chamber through a variable orifice in order to dilute the exhaust in the chamber as desired and to maintain a dynamic flow system. The air was purified by filtration through glass fiber filters, and a bed of activated charcoal. Irradiation of the chamber was accomplished by natural sunlight.

RESULTS AND DISCUSSION

Atmospheric aerosols

Each aerosol sample analyzed displayed two distinct cathodic steps, also termed reduction waves. Fig. 1 represents a typical atmospheric aerosol polarogram. In most instances, the observed diffusion current varied considerably among samples, indicating differences in the concentration of the constituents. However, half wave potentials, which were quite stable in position, always appeared at −0·425 ±0·020 and −1·030 ±0·070 V, indicating that not more than two substances were being determined.

Under the conditions of the experiments, the only inorganic materials likely to account for the observed waves were lead and zinc. Lead was found to be the cause of the wave at $E_{\frac{1}{2}} = -0{\cdot}425$ V, but zinc, which becomes evident at approximately −1·20 V in most alkali chloride electrolytes, was not found to be the causative agent of the second wave at −1·030 V. Polarographic identification of unknown substances

* Sargent Corp., Chicago, Illinois.

may be aided by adding quantities of known materials to solutions of the unknown. If the resulting polarograms exhibit identical waves of increased step height, identification is considered confirmatory (MILNER, 1957, p. 107). The cathodic step attributed to lead responded in a positive manner to the addition of lead ions to unknown solutions, but the addition of zinc ions resulted in the appearance of a zinc step in addition to the unknown atmospheric substance. Also, lead had been found to be present in quantity by emission spectrographic analysis. Moreover, the wave at −1·030 V was usually a very large cathodic step of much greater magnitude than the −0·425 V step, making it unlikely that zinc was responsible. The authors considered the possibility that a local source of emission peculiar to the Vernon sampling area (Vernon, California, laboratories of the Los Angeles County Air Pollution Control District) might be responsible for the second polarographic wave. However, identical wave structure was observed with samples obtained from other areas in Los Angeles County.

With the co-operation of the Robert A. Taft Engineering Center of the U.S. Public Health Service at Cincinnati, samples of aerosols for polarographic analysis were procured from other urban areas in the United States and also from London, England. Reproduced in Figs. 2, 3 and 4 are the polarograms of these samples. In all cases the aerosol samples exhibited identical qualitative polarographic structure. This may indicate that the aerosol components collected from polluted atmospheres of different urban areas have major properties in common.

As previously noted, major differences in wave height, particularly with respect to the second wave, were noted among samples. Atmospheric aerosol samples were collected at the Vernon sampling station on a time schedule to ascertain whether a correlation existed between the polarographic wave heights and simultaneous measurements of other pollutants associated with smog. For this purpose aerosol samples were collected and analyzed daily during a 12-month period from June 1957 through May 1958.

Comparison of the height of the second wave with concentration measurements of aldehydes, NO_2, ozone and eye irritation during the period under study yielded no useful correlations. As generally observed in the measurements of other pollutants, the wave heights increased during smog episodes and decreased in the absence of smog. In a limited number of samples compared, wave amplitudes were proportional to the weights of ether-soluble aerosols. When wave heights were compared with eye irritation, it was noted that in the majority of cases large wave amplitudes coincided with high intensities of eye irritation ; however, in a number of instances, large amplitudes were observed in the absence of eye irritation (ORCUTT, 1958). The fact that wave height did not always correlate with eye irritation was not entirely unexpected. Based on experimental work performed and described later, the possibility exists that organic nitro compounds of various types are responsible for the second wave polarograms and not necessarily all of these types would be eye irritants. Many of these substances may be toxic, however, and their polarographic measurement may be as important as the estimation of pollutants by the eye-irritation method.

The possibility was also considered that the second wave might be due to an organo-metallic compound consisting of lead in combination with organic substituents. This hypothesis was disproved by the fact that the two waves did not occur in any

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fixed ratio, and that lead was often completely absent even when a large second wave was observed.

Automotive exhaust aerosols

Inasmuch as automotive exhausts are responsible for the major portion of air pollutants in the Los Angeles area, it was felt that experiments with aerosol-forming

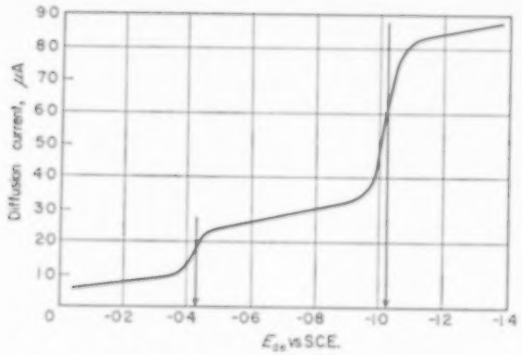

FIG. 1. Polarogram of aerosol sample from the Los Angeles atmosphere ; 6 September 1957 ; 0800–1000 hours.

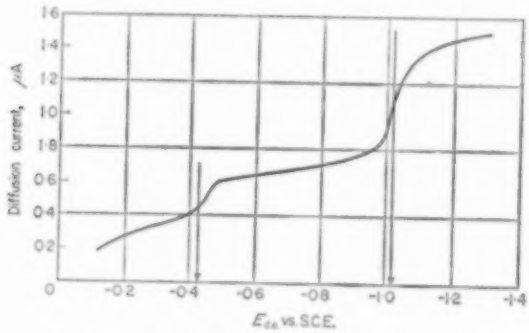

FIG. 2. Polarogram of aerosol sample from the London atmosphere · 5 January 1956.

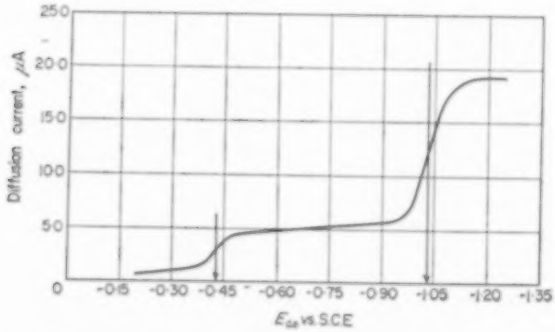

FIG. 3. Polarogram of aerosol sample from the Cincinnati atmosphere ; 25 November 1957.

exhausts might produce information as to the origin and chemical nature of the material causing the second wave.

Fig. 5 depicts a typical polarogram of irradiated auto aerosols from the International Harvester engine using a high olefinic fuel. It is evident from the current–voltage

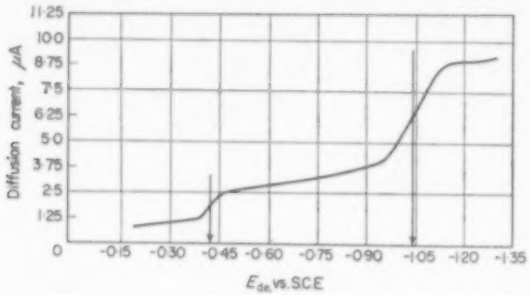

FIG. 4. Polarogram of aerosol sample from the Philadelphia atmosphere ; 20 November 1957.

relationship, that these aerosols are very similar, if not identical, in composition to atmospheric aerosols. Samples of the chamber atmosphere without exhaust yielded no polarograms. In addition, when ozone and NO_2 were introduced into the chamber in the absence of auto exhaust, no polarograms resulted.

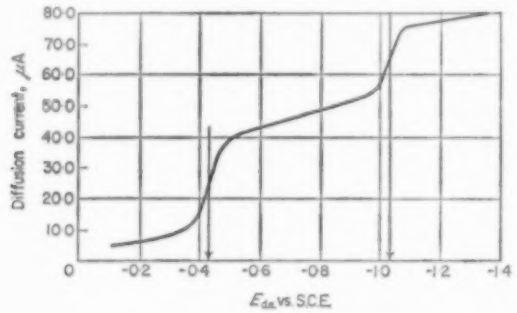

FIG. 5. Polarogram of aerosol samples from the Plexiglas chamber using olefinic fuel.

Exhaust aerosols from different fuels

A series of experiments was performed to determine whether differences in fuel composition would result in quantitative polarographic differences in the aerosols produced. The fuels selected for this work were a gasoline containing less than 1 per cent olefins and a blend of gasolines containing 34·7 per cent olefins. The polarographic comparison of the engine exhaust aerosols produced with different fuels was based upon diffusion current values per sampling time interval per unit of hydrocarbon present, according to the following :

$$\frac{\text{Diffusion current (microamperes)}}{\text{Sampling time (minutes)}} = \text{microamperes per minute}$$

and

$$\frac{\text{Microamperes per minute}}{\text{Hydrocarbon concentration (p.p.m.)}} = K.$$

Since the diffusion current is proportional to the quantity of unknown substance present and the amount of unknown substance probably is a function of hydrocarbon concentration and sampling time ; *K*-values, or the active aerosol constituents can be conveniently compared.

Summarized in Table 1 are diffusion current–time ratios, hydrocarbon concentrations, and *K*-values for each experiment performed using the International Harvester engine.

TABLE 1. A POLAROGRAPHIC COMPARISON OF IRRADIATED AUTOMOTIVE EXHAUST AEROSOLS FROM NON-OLEFINIC AND OLEFINIC GASOLINES IN THE INTERNATIONAL HARVESTER ENGINE

Gasoline	Microamperes per minute	Hydrocarbon concentration (p.p.m.)	*K*-Value
Olefinic (34·7%)	0·06	9	0·0066
"	0·07	11	0·0063
"	0·09	17	0·0053
"	0·05	44	0·0140
"	0·14	30	0·0047
Non-olefinic (less than 1%)	0·01	28	0·0004
"	0·03	19	0·0016
"	0·05	21	0·0024
"	0·01	35	0·0003
"	0·02	17	0·0011

The average *K*-values obtained for aerosols from the olefinic and non-olefinic fuels were 0·0074 and 0·0012 respectively. Hence, for these experiments, approximately six times the diffusion current (wave height) at the −1·030 V step was produced by the olefinic fuel compared with the non-olefinic.

A second series of experiments was performed in a similar manner with the use of a Fairbanks Morse two-cylinder engine as an exhaust source. The results of these runs are summarized in Table 2.

In these experiments *K*-values for non-olefinic fuel are zero since in all cases no diffusion current was produced, whereas distinct polarographic waves occurred with olefinic fuel. All samples produced a distinct metallic lead wave which approximately reflected the hydrocarbon concentration of the chamber, thereby indicating that the exhaust producing and aerosol sampling methods were functioning properly. These experiments lead to the following conclusions :

(1) Aerosols responsible for the second polarographic wave can be produced from automotive exhaust.
(2) A fuel high in olefin content produces a greater amount of these aerosols than a non-olefinic fuel under the defined experimental conditions.

Identification of aerosol constituents

Many experiments have been performed in attempts to define the chemical structure of the aerosols discussed in this report.

Samples of pure olefins (e.g. 1-hexene, 2-hexene, 1-heptene) exhibited no polarographic wave and yielded no waves when oxidized with oxygen or ozone. However,

when NO_2 was passed through liquid olefins the resulting reaction products yielded very strong waves in the −1·030 V region. Similarly, high olefinic gasoline treated with NO_2 yielded strong waves in the same region whereas gasoline with less than 1·0 per cent olefins similarly treated, yielded very slight waves. These results can be attributed to the fact that olefins react readily with NO_2, whereas straight chain paraffins and aromatic compounds react very slowly under identical conditions. These observations lend support to the possibility that the −1·030 V wave is associated with $(NO)_x$–olefin reaction products.

TABLE 2. A POLAROGRAPHIC COMPARISON OF IRRADIATED AUTOMOTIVE EXHAUST AEROSOLS FROM OLEFINIC AND NON-OLEFINIC FUELS IN THE FAIRBANKS MORSE ENGINE

Gasoline	Microamperes per minute	Hydrocarbon concentration (p.p.m.)	*K*-value
Olefinic (34·7%)	0·03	9·5	0·0032
,,	0·03	8·5	0·0035
,,	0·03	5·8	0·0052
,,	0·02	11·3	0·0017
,,	0·02	21·1	0·0009
,,	0·02	1·8	0·0111
Non-olefinic (less than 1%)	0·000	2·6	—
,,	0·00	2·1	—
,,	0·00	6·9	—
,,	0·00	12·2	—
,,	0·00	10·3	—

The addition of inorganic nitro compounds such as sodium nitrate, sodium nitrite and lead nitrate to automotive exhaust or atmospheric aerosols in solution, resulted in the formation of additional waves thereby excluding the possibility that the aerosols might consist of inorganic nitro compounds.

All available evidence indicates that both atmospheric and automotive exhaust aerosols contain organic nitro compounds. The general polarographic behavior of the aerosols is consistent with that of organic nitro compounds described in the literature. This is supported by the observation that no current–voltage curve is obtained when these aerosol samples are rendered alkaline, because of the formation of the aci-form of the compounds which is not electro-reducible (MILNER, 1957, p. 549–551).

SUMMARY

(1) Aerosols collected from polluted atmospheres of different urban areas exhibited identical qualitative polarographic structure. This may indicate that the aerosol components from the sampled atmospheres have major properties in common.

(2) Aerosols with the same polarographic characteristics were obtained from irradiated automotive exhausts.

(3) Fuels with high olefinic content produced large quantities of these aerosols, while low olefinic fuels gave rise to small amounts of the electro-reducible aerosols.

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(4) The chemical identity of the second wave forming substance has not been fully confirmed ; however, the experimental evidence indicates that the wave is associated with $(NO)_x$–olefin reaction products.

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We are indebted to the compilers of the sources from which the titles listed in this bibliography are selected. The number of papers published is so large that we considered a selection of the more important papers made by one with great experience in the field of air pollution would be of considerable value, a task kindly undertaken by Mr. T. F. Hurley.

Abstracts of the papers listed can be found in *A.P.C.A. Abstracts* Jan.-Sept. 1959 (denoted by " A " and code number) or *Public Health Engineering Abstracts* June-Aug. 1959 (denoted by " P "). In future issues of the journal, selected titles from three months of abstracts will be listed.

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Notes and News

Anniversary of the Staubforschungs-Institut

THE **Staubforschungs-Institut** in Bonn, which recently celebrated the twenty-fifth anniversary of its establishment, has commemorated this event with the publication of a book describing its past history and present activities.*

The institute was founded in 1934, with its first headquarters in Berlin, by ARNOLD LÄMMERT. For the preceding 2 years LÄMMERT had been studying dusts in quarrying under the auspices of the German quarry-owners association, who were gravely concerned at the high incidence of silicosis in this industry. Its aim was to investigate both the physiological action on the human body of dusts and fumes from industrial processes and the causes of and means of combating the formation of such fumes and dusts in industry generally. Together with his associates, LÄMMERT carried out investigations in a wide variety of industries in which dusts affect the health of the workers until 1939, when, with the advent of war, the activities of the institute were restricted. With the destruction of its building, apparatus and records, the work ceased in 1944. In 1948, however, LÄMMERT was able to resume his work in rented apartments in Bonn, where he continued until his retirement in 1953, at the age of 70. He was succeeded by Dr. A. WINKEL, who is the present head of the institute. To house the growing institute a new building was erected in 1954, and it is hoped that this will prove adequate for a number of years.

The work of the institute is divided into five departments, of which the general activities and some of the more outstanding achievements are outlined here.

The department for physical measurements, headed by Dr. D. HASENCLEVER, which specializes in dust sampling and measurement, has designed a new type of konimeter which has been widely adopted by industry in Western Europe. Large numbers of particle size analyses have been undertaken, and more recently, methods have been developed with which extremely small concentrations of radioactive particles in air can be detected. Extensive facilities are also available for testing filter materials, gas masks and industrial protective clothing.

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The department for chemical and mineralogical investigations, led by Dr. K. G. SCHMIDT, carries out numerous chemical analyses of dusts. An exact method has been evolved for the accurate determination of silicic acid based on the principle that in hot phosphoric acid (250°C) silicates dissolve, but quartz, tridymite or crystobalite are not attacked. Phase contrast microscopy has also been developed to such an extent that the various types of mineral dust particles, even as small as 1μ can be quantitatively estimated by counting in the same sample ; e.g. it is possible to differentiate between pumice of different origins such as Lipari and Germany, the former of which is harmful.

Mr. E. WALTER heads the department for ventilation research. This section has equipment for testing industrial dedusting plant (bag filters, electrostatic precipitators, etc.) using standard test dusts with volume flow rates as high as 2000 m³/hr. It also carries out experiments on exhaust hoods and the ventilation of factories where dangerous dusts are formed in processing.

In addition to investigating the explosive limits of dust air mixtures, Mr. G. KÜHNEN has made a particular study of situations, which, although in themselves not dangerous, can lead to explosions. Mr. KÜHNEN has also specialized in microanalytical techniques for dust analyses.

Mr. A. SCHÜTZ, who has been working on the brown fumes from oxygen lancing processes in steel making, has developed an ingenious method of obtaining in the laboratory a reproducible fume identical with furnace fumes, by means of an electric arc between carbon electrodes filled with iron filings. At present he is attempting to use polarization effects in agglomerating the fine fume particles at high temperatures in electric fields, as well as establishing the temperature limitations for more conventional types of electrostatic precipitators.

Perhaps the most important activity of the institute which affects workers in the air pollution field outside Western Europe is the publication of the journal *Staub*, which is edited by the institute's director, Dr. WINKEL and by Mr. SCHÜTZ. *Staub*, first issued in 1936, was published irregularly until 1944 and again from 1950 onwards, but since January 1958 has appeared monthly. Besides its many research papers and technical reviews, *Staub* has, since its inception, abstracted from other journals

* *25 Jahre Staubforschungs-Institut des Hauptverbandes der Gewerblichen Berufsgenossenschaften.* Bonn, Langwartweg 103, Germany, 1959. 47 pp.

over 6000 papers to the general fields of dust technology, air pollution and the physiology of pneumoconiosis. These abstracts, many of considerable length, have attempted to give a comprehensive review of the original papers, which often appeared in obscure journals, thus making reference to the original unnecessary.

This outline will indicate to those active in air pollution studies the debt owed to the invaluable work of the Staubforschungs-Institut both directly by industry in Western Europe and more generally by the publication of *Staub*. The present writer would like to add his congratulations on the institute's twenty-fifth anniversary.

W. STRAUSS

Strontium-90-Symposium in Bad Kreuznach/Deutschland

VOM 28–31 Oktober 1959 veranstaltete der " Sonderausschuss Radioaktivität " in Bad Kreuznach ein Symposium über die neuesten Forschungsergebnisse des Radiostrontiumproblems. Namhafte Experten des In- und Auslandes diskutierten die verschiedenen Problemkreise.

Zu dem Problem der Verweilszeiten in der Stratosphäre berichtete Prof. SPAR, New York über neueste Messergebnisse, die im Rahmen eines mehrjährigen Forschungsprogramms (" Project High Altitude Sampling Program ") erhalten wurden. Die Ergebnisse führen zu dem Schluß, daß die Verweilszeiten von Sr^{90} in der Stratosphäre offenbar wesentlich kürzer sind als bisher angenommen wurde. Während man bisher mit Verweilszeiten von 5–10 Jahren rechnete, führen SPAR's Untersuchungen auf Verweilszeiten von der Größenordnung 1 Jahr. Die Verweilszeit ist außerdem eine Funktion der geographischen Breite.

Dr. RUSSELL, Groß-Britannien schilderte neue Ergebnisse über den Mechanismus der Sr^{90} Aufnahme. Etwa 65 Prozent des Radiostrontium in menschlichen Körper stammen aus der Milch und den Milchprodukten. Aus dem Vergleich des Verhältnisses von Strontium 89 zu Strontium 90 in der Milch und im Niederschlag ergab sich, daß das Sr^{90} im Sommer 1–2 Monate braucht, um vom Regen in die Milch zu gelangen. Gleichzeitig wurde gefunden, daß das Sr^{90} der Pflanzen zum überwiegenden Teil durch die Blätter aufgenommen wird.

Fragen über Messmethoden, Gehalt des menschlichen Skeletts an Sr^{90}, Dekorporierung und maximal zulässiger Konzentrationen waren ebenfalls Themen der Vorträge und Diskussionen.

Die gehaltenen Vorträge sowie die Diskussionen werden im Laufe des nächsten Jahres voraussichtlich in der Schriftenreihe des Bundesministeriums für Atomkernenergie und Wasserwirtschaft veröffentlicht werden.

W. KLUG

Stanford Research Institute Symposium in San Francisco

STANFORD RESEARCH INSTITUTE will sponsor a " Symposium on Chemical Reactions in the Lower and Upper Atmosphere " from April 18–20, 1961, at the Mark Hopkins Hotel in San Francisco. Correspondence should be directed to R. D. CADLE, Stanford Research Institute, Menlo Park, Calif.

CHARLES ELKIND

Air Poll. Pergamon Press 1960, Vol. 2, p. 301. Printed in Great Britain.

Book Reviews

Atmospheric Chemistry of Chlorine and Sulphur Compounds. Edited by J. P. LODGE.

THIS well produced volume of about 130 pages is the third Geophysical Monograph published by the American Geophysical Union of the National Research Council and is the record of papers presented and discussed at the Robert A. Taft Sanitary Engineering Center, Cincinnati, in November, 1957.

The twenty-four papers are varied in quality and length and are covered in four sections dealing with analytical methods, field techniques and engineering control, urban concentrations and distribution of pollutants. Most of them are important original studies; others are summaries of work published elsewhere.

The presence of chloride and sulphate in air is fully discussed and the rôle of the oxides of sulphur and the oxides of nitrogen and nitrides in the final equilibrium in the air is considered. Particulate studies have revealed sodium chloride, calcium sulphate and ammonium sulphate as crystalline constituents of atmospheric solids.

In all, twenty-seven pages are given over to verbatim addresses of welcome and discussions with a full list of names and addresses of the conference members. With so small a volume and such brief summaries of some papers one wonders if this space could have been better devoted, in part, to fuller summaries or even reprints of the summarized papers. There is, however, no doubt that this monograph is an important contribution to knowledge of atmospheric chemistry and that all workers in this field should have access to it.

A. J. LINDSEY

ERRATUM

R. Trappenberg: Die Ansbreitung von Staub und Gas nach Sutton. *Int. J. Air Poll.*, **2**, 27–41.

on p. 33 Abb. 2 4 m/sec should read 6 m/sec
Abb. 3 6 m/sec should read 4 m/sec

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PAPERS ACCEPTED FOR PUBLICATION

N. A. RENZETTI and GEORGE J. DOYLE: Photochemical aerosol formation in sulfur dioxide-hydrocarbon systems.

HERBERT E. STOKINGER: Toxicological interactions of mixtures of air pollutants. Review of recent developments.

P. J. MEADE: The estimation of ground-level concentrations from an elevated source.

JAMES P. LODGE Jr., GEORGE S. BIEN and HANS E. SUESS: The carbon-14 content of urban airborne particulate matter.

R. A. BAGNOLD: The re-entrainment of settled dusts.

MARY O. AMDUR: The response of guinea pigs to inhalation of formaldehyde and formic acid alone and with a sodium chloride aerosol.

W. KLUG: Air pollution research in West Germany.

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Int. J. Air Poll. Pergamon Press 1960. Vol. 2, pp. 303–308. Printed in Great Britain.

THE ESTIMATION OF GROUND LEVEL CONCENTRATION FROM AN ELEVATED SOURCE*

P. J. MEADE
Meteorological Office, Kingsway, London, W.C. 2
(*Received* 21 *October* 1959)

Abstract—SUTTON's equations for calculating ground level concentrations of gases or dusts of negligible fall speed due to an elevated source are put into a convenient non-dimensional form. This is done by incorporating in the equations the maximum value of the concentration and the distance along the axis of the plume where this maximum occurs. It is then shown how for each value of the stability parameter, n, a single curve gives the distribution of concentration along the axis and a single diagram gives the distribution of concentration over the whole area downwind of the source, for any values of the remaining parameters in SUTTON's equations. The use of the curve and the diagram will avoid the necessity of lengthy computations involving exponential factors and alternative values of several parameters.

SUTTON (1) has given the following expression for the concentration at ground level due to a continuous source at a height h in the atmosphere.

$$C = \frac{2Q}{\pi C_y C_z u x^{2-n}} \exp\left(\frac{y^2}{C_y^2 x^{2-n}}\right) \exp\left(-\frac{h^2}{C_z^2 x^{2-n}}\right) \tag{1}$$

In this expression :

- C is the concentration in g/cm^3
- Q is the source strength in g/sec
- u is the horizontal wind speed, assumed constant, in cm/sec
- x is the horizontal distance downwind from the base of the source
- y is the horizontal cross-wind distance
- n is a stability parameter
- C_y is a diffusion coefficient for lateral spreading
- C_z is a diffusion coefficient for vertical spreading.

At ground level along the axis of the plume $y = 0$ and the axial concentration C_a is then, from equation (1), given by

$$C_a = \frac{2Q}{\pi C_y C_z u x^{2-n}} \exp\left(-\frac{h^2}{C_z^2 x^{2-n}}\right) \tag{2}$$

By inspection of equation (1) it is clear that the maximum ground level concentration C_m occurs somewhere on the axis of the plume and, by differentiation of equation (2), it can be shown that

$$C_m = \frac{2Q}{e\pi u h^2}\left(\frac{C_z}{C_y}\right) \tag{3}$$

* After the above paper was submitted for publication the writer's attention was drawn to a paper by Falk *et al.* (Pittsburg, Pa., Air Repair, 4, 1954, pp. 87–95) in which experimental work on the dispersion of effluent from a stack was analysed and discussed. In this latter paper the Bosanquet and Pearson formula for concentration is used and for axial concentrations a non-dimensional technique is derived on similar lines to that described above for the Sutton formula. The two papers use different approaches, however, in the treatment of area concentrations.

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and the distance x_m from the base of the source where the maximum concentration occurs is

$$x_m = \left(\frac{h}{C_z}\right)^{2/(2-n)}. \tag{4}$$

In equation (3) e is the base of Napierian logarithms, i.e. 2·72 approximately.

The above equations are generally used when estimations of likely concentrations are required in connexion with the emission of effluent from an existing stack or a projected one, of which the height h and other parameters are under consideration. Equations (3) and (4) provide a convenient means of estimating maximum concentrations and the point where they will be found, but equations (1) and (2), which give the distribution of concentration over an area and along the plume's axis, are somewhat involved and many separate computations may be necessary to cover all the probable values of the different parameters. The procedure described below largely overcomes these objections.

DISTRIBUTION OF CONCENTRATION ALONG THE AXIS OF THE PLUME

Equation (2) gives the distribution of concentration along the plume's axis. Dividing this equation by equation (3) and using the results of equation (4), we obtain

$$\frac{C_a}{C_m} = e\left(\frac{x_m}{x}\right)^{2-n} \exp\left\{-\left(\frac{x_m}{x}\right)^{2-n}\right\}. \tag{5}$$

It will be noted that equation (5) is in non-dimensional form and does not contain explicitly the wind velocity u, the effective height of the plume h, or the diffusion

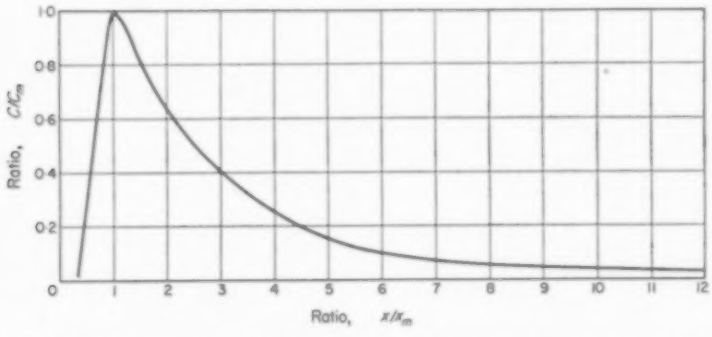

FIG. 1. Ground level concentrations (C) as a fraction of the maximum concentration (C_m) along the axis of the plume from an elevated source. (Neutral atmospheric conditions.)

coefficients C_y and C_z. These parameters are, of course, required for the calculation of C_m and x_m, by means of equations (3) and (4), but are not required thereafter for calculations of the distribution of concentration. In fact, if the stability parameter n is known, equation (5) provides a unique and simple expression for the pattern of axial concentration, whatever the values of u, h, C_y and C_z.

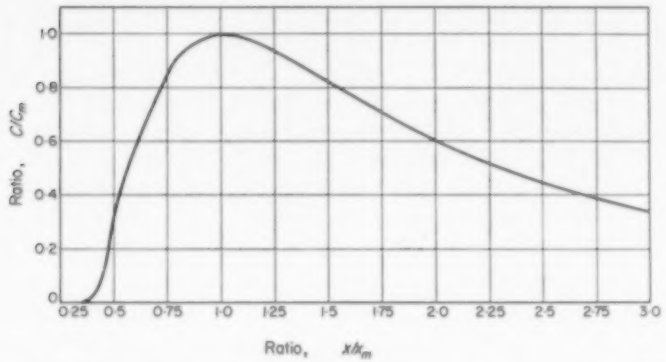

FIG. 1A. Ground level concentrations (C) as a fraction of the maximum concentration (C_m) along the axis of the plume from an elevated source. (Neutral atmospheric conditions.)

Note : The above curve is taken from Fig. 1 for the range of distance $0 < \frac{x}{x_m} \leqslant 3$ but with a more open scale.

Fig. 1 is the curve represented by equation (5) for conditions of neutral stability in the atmosphere with $n = 0{\cdot}25$ and, as will be seen, distances from the base of the source are indicated by x/x_m, their ratio to the distance where the maximum concentration occurs. Similarly the ordinate gives the concentration as a ratio, C_a/C_m, to the maximum value. Fig. 1A is a portion of the curve in Fig. 1 for values of x/x_m equal to 3 or less, but drawn with a more open scale over the region in which the relative concentration C/C_m varies rapidly.

In any particular case, therefore, with the parameters u, h, C_y and C_z given or estimated, it is only necessary to calculate C_m and x_m from equations (3) and (4). Then Figs. 1 and 1A give the distribution of pollution and the corresponding values of C_a and x are readily derived.

DISTRIBUTION OF CONCENTRATION OVER AN AREA

As is indicated by equations (1) and (2), off-axis concentrations are related to the axial concentration C_a at the same downwind distance x by the exponential factor.

$$\exp\left(-\frac{y^2}{C_y^2 x^{2-n}}\right)$$

This factor contains the lateral diffusion coefficient C_y. If the turbulence is isotropic $C_y = C_z$, but these conditions do not usually apply in the layer of atmosphere near the ground. We therefore write

$$C_y = \alpha C_z \tag{7}$$

where α is a number, and using a similar analysis to that already described, equation (1) may be written in the form

$$\frac{C}{C_m} = e\left(\frac{x_m}{x}\right)^{2-n} \exp\left\{-\left(\frac{x_m}{x}\right)^{2-n}\right\} \exp\left\{-\frac{y^2}{\alpha^2 h^2}\left(\frac{x_m}{x}\right)^{2-n}\right\}$$

$$= \frac{C_a}{C_m} \exp\left\{-\frac{y^2}{\alpha^2 h^2}\left(\frac{x_m}{x}\right)^{2-n}\right\} \tag{8}$$

In equation (8), compared with equation (5), the only new parameters that appear are the cross-wind distance y and the ratio of C_y to C_z, i.e. α. As before, therefore, once

C_m and x_m have been calculated, a unique curve provides the distribution of pollution over an area for each value of the stability parameter n.

For purposes of illustration and also because it represents the most realistic application, we again choose $n=0{\cdot}25$ corresponding to neutral atmospheric stability. A representative value of α is also required. On the basis of numerous field experiments carried out over level downland at Porton, SUTTON (1953) has given values of C_y and C_z which indicate that α has the value 2, a figure which appears to be confirmed by later work over the same terrain. We therefore choose this value of α together with $n=0{\cdot}25$ for substitution in equation (8) and the resulting curves for $C/C_m=1/2$, $1/5$ and $1/10$ are shown in Fig. 2.

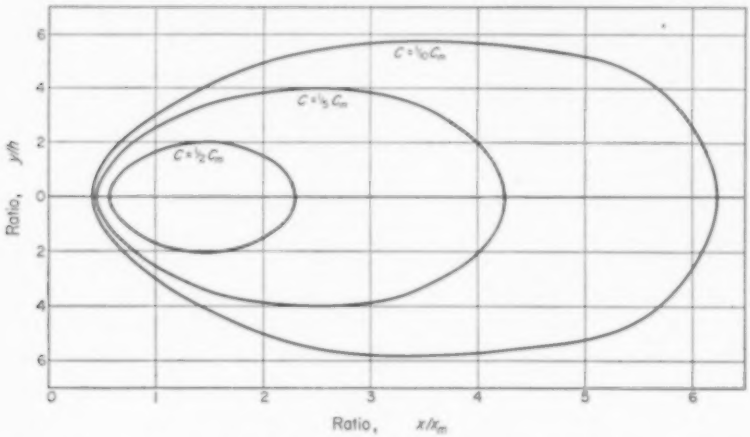

FIG. 2. The distribution over an area of ground level concentrations (C) due to an elevated source of height h. (Neutral atmospheric conditions.)

In Fig. 2, downwind distances are given by x/x_m, as in Fig. 1, but cross-wind distances are given by their ratio to h, the effective height of the source. For neutral conditions and with the assumed value of α, therefore, Fig. 2 gives the distribution of concentrations over an area whatever the values of the parameters u, h and C_y (or C_z). The point of maximum concentration is given by the coordinates :

$$\frac{x}{x_m}=1 \quad \text{and} \quad y/h=0.$$

The curves in Fig. 2 may also be used if the ratio C_y/C_z is not equal to 2 but then the ordinate scale for y/h would have to be adjusted. It is important to take account of this possibility because over terrain different from that at Porton different values of C_y and C_z would generally be found. For example, over rough hilly country at Oak Ridge, U.S.A., HOLLAND (1953) found C_y and C_z approximately equal, i.e. $\alpha=1$. For this value of α, it is only necessary to amend the ordinate scale by inserting 1.2 and 3 in place of 2, 4 and 6 respectively before using the concentration curves.

APPENDIX

Some Practical Examples

In the presentation above, equations (1)–(4) are in c.g.s. units and equations (5) and (8) which are plotted in Figs. 1, 1A and 2 for $n=0{\cdot}25$, are non-dimensional. Before using the figures, however, it is

necessary to evaluate C_m and x_m from equations (3) and (4) respectively. It will be convenient, therefore, to express these equations in units commonly used for everyday purposes.

Let Q = strength of source in tons/day,
h = effective height of source in feet,
u = horizontal wind speed in miles/hr,
x = horizontal distance downwind from the base of the source in yards.

In addition, the diffusion coefficients C_y and C_z are to be expressed in units of $(\text{ft})^{n/2}$. To conform with Figs. 1, 1A and 2, we take $n = 0{\cdot}25$ and using values given by SUTTON (1953),

$$C_y = 0{\cdot}4 \text{ cm}^{1/8} = 0{\cdot}26 \text{ ft}^{1/8}$$
$$C_z = 0{\cdot}2 \text{ cm}^{1/8} = 0{\cdot}13 \text{ ft}^{1/8}.$$

Then, with Q in tons/day, h in feet and u in miles/hr,

$$C_m = 3{\cdot}25 \times 10^6 \frac{Q}{uh^2} \text{ mg/100 m}^3 \tag{9}$$

If the pollutant is sulphur dioxide,

2·86 mg SO_2/100 m³ is equivalent to 1 part/100 million parts of air.

Then
$$C_m = 1{\cdot}14 \times 10^6 \frac{Q}{uh^2} \text{ p.p.h.m. (parts per 100 million).} \tag{10}$$

Also, from equation (4),

$$x_m = \frac{1}{3}\left(\frac{h}{C_z}\right)^{8/7} \text{ yd.} \tag{11}$$

It is to be emphasized that h, the effective height of the source, is the sum of the chimney height and the additional height imparted to the plume by means of buoyancy and efflux velocity. Methods for calculating h have been given by HOLLAND (1953), BOSANQUET (1957), SCORER (1959) and in other papers.

Example 1

Suppose the effective height of a source is 100 ft, that the output of SO_2 is 1 ton/day and that the wind speed is generally 5 miles/hr or more. Since greater wind speeds give lower concentrations, we use 5 miles/hr to estimate the maximum.

From (10) and (11)

$$C_m = 23 \text{ p.p.h.m.}$$
$$x_m = 660 \text{ yd.}$$

Using Fig. 1, ground level concentrations along the axis would exceed 2·3 p.p.h.m., i.e. one-tenth the maximum, within distances given by

$$0{\cdot}4 < x/x_m < 6{\cdot}1$$

i.e. within the range 260 yd to 4030 yd from the stack.

The range within which concentrations along the axis would exceed 15 p.p.h.m. is given by

$$x/x_m = \frac{15}{23} = 0{\cdot}65 \text{ (approx).}$$

Using Fig. 1A, this range is found to be from about 400 yd to about 1260 yd.

The width of the plume for specified concentration limits can be estimated from Fig. 2. Concentrations greater than 2·3 p.p.h.m. may occur up to distances from the axis given by

$$y/h = 5{\cdot}6$$

i.e.
$$y = 190 \text{ yd (approx).}$$

Thus concentrations greater than 0·1 C_m may be found at distances up to about 190 yd on each side of the plume's axis.

Similarly it may be estimated by extrapolation in Fig. 2 that concentrations greater than 15 p.p.h.m. may occur at distances up to about 40 yd on each side of the axis.

Example 2

A chimney with an output of 15 tons SO_2/day is planned in an area where the wind speed exceeds 7 miles/hr on 60 per cent of occasions and exceeds 3 miles/hr on 85 per cent of occasions. Estimate

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the effective height of the source if the maximum ground level concentration is not to exceed 50 p.p.h.m. (a) for winds of 7 miles/hr or more and (b) for winds of 3 miles/hr or more.

(a) Winds 7 miles/hr or more

From (10)

$$50 = \frac{1{\cdot}14 \times 10^6 \times 15}{7h^2}$$

giving $h = 225$ ft (approx)

and $x_m = 1700$ yd (approx).

Thus, if the chimney is to be 100 ft high, the effluent gases should have sufficient efflux velocity and buoyancy to gain an additional 125 ft in height.

(b) Winds 3 miles/hr or more

From (10)

$$50 = \frac{1{\cdot}14 \times 10^6 \times 15}{3h^2}$$

giving $h = 340$ ft (approx)

and $x_m = 2700$ yd (approx).

Acknowledgement—This note is published with the permission of the Director General of the Meteorological Office.

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THE CARBON-14 CONTENT OF URBAN AIRBORNE PARTICULATE MATTER*

JAMES P. LODGE Jr.†, GEORGE S. BIEN‡ and HANS E. SUESS‡

(*Received* 28 *October* 1959)

Abstract—Very large samples of atmospheric particulate matter were collected in the central part of St. Louis, Missouri and Los Angeles, California. The carbon-14 content of various fractions of the samples was determined, and was interpreted in terms of the relative contribution of fossil fuels and contemporaneous sources of carbon to the particulate pollution of the area. It can be shown by this method, for example, that substantially all of the aliphatic hydrocarbons in the samples are of fossil origin, while about one-fourth of the oxygenated materials are derived from living matter. The general applicability of the method is discussed.

INTRODUCTION

IT IS well known that living substances are in equilibrium with the content of radioactive carbon-14 in the ambient atmosphere. This carbon is formed primarily in the stratosphere by (n,p) reaction with nitrogen-14, and is subsequently completely mixed with the general atmosphere in the form of carbon dioxide.

When an organism ceases to live, it ceases to exchange carbon with the atmosphere. Its carbon-14 content thereafter decreases in the manner dictated by its half-life of approximately 5700 years. This fact is utilized in determining the ages of archeological objects, as described by LIBBY (1955) and others. The fossil fuels coal, petroleum and natural gas, although formed from organic substances, are of such great age that their carbon-14 content is substantially nil.

The carbonaceous material contained in particulate material from urban atmospheres arises primarily from two types of source. The first is the combustion of fossil fuels. Particulate matter from this source contains no radioactive carbon. On the other hand, the combustion of wood, paper, garbage and other sorts of refuse gives rise to particulate matter containing carbon of substantially the same isotopic composition as that of living matter. Pollens, micro-organisms, plant debris, and similar material also contribute to the "live" carbon content of particulate collections. The sources of carbon of an age intermediate between these two extremes are negligible. Consequently, the isotopic composition of carbon from polluted atmospheres can be interpreted, not in terms of age, but in terms of the relative contributions of fossil fuel and contemporaneous material to the overall atmospheric pollution complex.

This relationship was first explored by CLAYTON *et. al.* (1955) who examined two large samples each from Detroit and Los Angeles. Since a large portion of any bulk

* Presented at 136th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1959.

† Chemical Research and Development, Air Pollution Engineering Research, Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati 26, Ohio.

‡ Division of Marine Geology and Geochemistry, Scripps Institution of Oceanography, University of California, La Jolla, California.

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sample consists of resuspended matter (ground paper, plant tissue, etc.) and soot, which cause nuisance, but which have less health significance than extractable materials, it seemed desirable to extend their measurements to fractionated samples.

No attempt was made to carry out an exhaustive study of variability, seasonal trends or geographical differences within a city. The project was aimed rather at determining the possible usefulness of the technique as a method of evaluating relative contributions from various sources of carbonaceous material. In this respect the research is similar to the work of CLAYTON *et al.*, and to that of TRUESDAIL (1958), who made a brief study of isotopic carbon distribution among gaseous pollutants.

Through the courtesy of Mr. FRANK A. PATTY of the General Motors Corporation, the large volume sampling device used in their studies was made available. Muffling devices were added to make it possible to operate the sampler in more densely populated areas. The city first chosen for study was St. Louis, Missouri. The sampler was located in Forest Park, a large municipal park located in a residential area in the middle of the metropolitan complex, approximately 7 miles from the downtown area. A total of seven samples was taken during the first 6 months of 1957. During April, 1958, a single large sample was taken in Los Angeles, using an array of eighteen high volume samplers situated on the roof of the laboratories of the Los Angeles County Air Pollution Control District in the Vernon area. Processing of the samples through the initial fractionation or other chemical handling was performed at Taft Sanitary Engineering Center in Cincinnati. Isotopic composition was determined using the facilities of the Scripps Institution of Oceanography.

EXPERIMENTAL

The sampler described by CLAYTON *et al.* (1955) was modified by the addition of a baffle chamber to reduce operating noise. The filter used was flash fired glass filter felt (Mine Safety Appliances Company) in sheets 2 ft × 10 ft. For each sample the sampler was operated for approximately 1 week at an average flow rate of approximately 1000 ft^3/min. Thus each sample represented the particulate matter from approximately 11 million ft^3 of air.

One sample was expended in preliminary studies. A second was used to determine the carbon and carbon-14 content analysis of the total sample. Two filters were each extracted with ether for 1 week using a large Soxhlet apparatus, and the carbon-14 contents of the extract and the residue on the filter were determined separately. The last three samples were extracted in like manner and their extracts pooled. This pooled ether extract was then separated on the basis of solubility in various solvents, as described by TABOR *et al.* (1958).

The 160 individual filters from Los Angeles were extracted together and fractionated as before. From a total of 128 g of particulate matter, only 7·62 g of extract was recovered. It was therefore not possible to replicate any of the determinations.

Carbon-14 content was determined by conversion to acetylene, according to the method of SUESS (1954). Residues on the filter were treated with acid to remove carbonate carbon before further processing. The accuracy of the determination of carbon-14 varied from 0·1 per cent to the order of 5 per cent, depending on sample size. A number of the determinations were made on samples containing markedly less than 1 g of carbon.

RESULTS AND DISCUSSION

The data obtained are summarized in Table 1. The activity determined is given in percentage of that of " standard " wood, i.e. of wood grown in the nineteenth century, at the time of its growth. Plant material actually growing at the time when the pollutant samples were taken had an activity of about 10 per cent above that of " standard " wood due to the presence in nature of C^{14} produced by nuclear explosions. This complication, however, in no way affects our conclusions. As indicated, the

TABLE 1. COMPOSITION OF ST. LOUIS (numbered) AND LOS ANGELES (LA) SAMPLES

Filter No.	Fraction	Wt. of[a] fraction (g)	Wt. of carbon[a] in fraction (g)	Percentage[a] contemporaneous carbon ± standard deviation
2+3+6	Extract	(3·87)	(2·26)	(14·4)
	Aliphatic neutral	1·12	0·57	< 5
	Aromatic neutral	0·87	0·61	8·3 ± 4
	Oxygenated neutral	0·67	0·41	25 ± 5
	Acid	1·21	(0·67)[b]	25 ± 5
4	Total	(6·37)[c]	3·82	22·6 ± 0·1
5	Total	(9·35)	(5·40)	(13·6)
	Extract	2·44	1·26	< 5
	Residue	(6·91)[c]	4·14	17·8 ± 1·1
7	Total	(9·83)	(5·86)	(27·0)
	Extract	2·91	1·71	19·8 ± 0·1
	Residue	(6·92)[c]	4·15	28·6 ± 0·1
LA	Total	(38·01)	(18·14)	(40·0)
	Extract	7·62	(3·84)	(14·5)
	Residue	(23·8)[c]	(14·30)	46·8 ± 2·0
	Aliphatic neutral	2·06	1·3	< 5
	Aromatic neutral	0·80	0·44	13·2 ± 6·0
	Oxygenated neutral	1·96	1·11	24·3 ± 5·0
	Acid	1·77	1·02	22·6 ± 5·0

(*a*) Values in parentheses are calculated rather than measured.

(*b*) Calculated from sample weight, assuming sample to be 55 per cent carbon; a portion of the sample was lost in processing.

(*c*) Calculated from weight of carbon, assuming sample to be 60 per cent carbon.

gross composition of most of the filters has been calculated from the activities and amounts of carbon in the individual fractions. It will be noted that the gross content of contemporaneous carbon in the original samples is somewhat variable. There is no clear correlation between carbon content and daily outdoor temperature range during the sample period, which might be expected to occur since low temperatures favor the combustion of larger amounts of fossil fuel. The table also displays the relative contribution to the overall activity of the various organic fractions. The " water soluble " and " basic " fractions (TABOR *et al.*, 1958) were too small for analysis. It will be noted that the residue insoluble in ether is more active than the ether-extracted

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material. This activity presumably reflects the presence in the residue of resuspended organic dusts such as ground paper, leaves, etc., which do not make a corresponding contribution to the extract. The various oxygenated materials (the acids and the oxygenated neutral compounds) have a somewhat higher activity than the total extract. A considerably larger percentage of the aromatic hydrocarbons, and almost all of the paraffinic material, are derived from fossil sources. This result is not unexpected, but has never previously been proven.

The data show that, while the gross samples from the two cities vary markedly, the pooled extracts and their fractions are quite similar. The principal difference, so far as the long-term mean is concerned, appears to lie in the residues. A possible hypothesis to explain the high activity in the Los Angeles residue lies in the fact that it was taken early in the dry season after an unusually wet winter. Thus an unusually heavy growth of vegetation was being dried out, ground underfoot, and resuspended in the air. It has been hoped that the Los Angeles samples would reflect the effects of the ban on domestic incineration. However, the absence of information on the composition of extractable material prior to the ban makes it improper to draw conclusions of this sort.

CONCLUSIONS

The isotopic composition of carbonaceous material in particulate samples taken from polluted atmospheres reflects the sources of this material. Distinctions among sources not possible by any other means than complete source inventory may be made by this method. The unfortunately large sample size required makes the technique expensive ; however, there are a number of situations in which no other approach will serve as well. The expected variation in isotopic content among the various fractions of particulate matter was observed with the activity varying in the order :

$$\text{Material insoluble in ether} > \left\{\begin{array}{l}\text{Total ether extract}\\ \text{Neutral oxygenated compounds}\\ \text{Acidic compounds}\end{array}\right\} > \begin{array}{l}\text{Neutral}\\ \text{aromatic}\\ \text{compounds}\end{array} > \begin{array}{l}\text{Neutral}\\ \text{aliphatic}\\ \text{compounds}\end{array}$$

Acknowledgements—Mr. ARTHUR C. STERN and Drs. LESLIE A. CHAMBERS and JAMES R. ARNOLD assisted in the planning of this experiment. The General Motors Corporation kindly donated the very large volume sampler used in the St. Louis study. Samples in St. Louis were taken under the direction of Mr. JEROME E. MOLOS, Acting Chief, Industrial Hygiene Section, St. Louis Department of Public Welfare. The Los Angeles samples were provided through the courtesy of Mr. J. C. ROMANOVSKY, Head, Air Monitoring Section, Los Angeles County Air Pollution Control District, 434 South San Pedro Street, Los Angeles. Extractions were performed by ARTHUR WARTBURG and JOHN SPILLE of the Sanitary Engineering Center. The carbon dating laboratory of Scripps Institution of Oceanography is maintained primarily by funds from the Atomic Energy Commission.

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TOXICOLOGIC INTERACTIONS OF MIXTURES OF AIR POLLUTANTS
REVIEW OF RECENT DEVELOPMENTS

HERBERT E. STOKINGER
U.S. Department of Health, Education, and Welfare
Public Health Service
Bureau of State Services
Occupational Health Program
1014 Broadway, Cincinnati 2, Ohio
(*Received* 18 *September* 1959)

Abstract—Recent developments are reviewed of laboratory research, stimulated by the Donora disaster a decade ago and more recently by the critical smog situation in Los Angeles, that has resulted in new findings and concepts of the interaction of certain components in both reducing and oxidizing smogs. In reducing smog in which SO_2 plays a dominant role, interaction with solid aerosols appears to go far in explaining the abnormal and unpredictable responses at Donora. Based on this and related work, a physicochemical theory has been developed that appears to offer a satisfactory explanation for most of these reactions.

On the other hand, physiologic mechanisms appear to govern interaction of those components of oxidant smog thus far studied. Three areas have been investigated:

(1) Tolerance and cross-tolerance among oxidant air pollutants.
(2) Protection by oil mists against ozone and nitrogen dioxide, and
(3) Antagonism of a variety of sulfur compounds for these oxidants.

Although each is a protective mechanism, all are believed to proceed by different physiologic pathways.

The nature and degree of protection is presented for each type of action, as well as hypothesis of the mechanisms in so far as biochemical investigation has indicated. An instance of striking synergism is also reported between ozone and hydrogen peroxide.

At least four significant contributions to our understanding of the acute short-term interactions of smog components have been made.

(1) A theory of physicochemical interaction, based on experimental work on the biological effect of mixtures of aerosols with gases and vapors, which provides a basis for predicting future abnormal response of synergism and antagonism among certain chemically or catalytically active smog components has been developed.

(2) Many oxidant smog combinations have been shown to possess the capacity to confer protection on the host against acute effects from further exposure and also to provide a cross-protection against chemically dissimilar oxidant smog components.

(3) The finding of marked similarity to radioprotective substances in the type of sulfur compounds that provide protection to animals against the acute effects of typical smog oxidants focuses attention on the radiomimetic properties of certain oxidants and brings into closer relationship the biologic effects of radiation and certain oxidant air pollutants.

(4) Oxidant smog mixtures derived from petroleum combustion appear to contain some components that are mutually antagonistic physiologically against the short-term effects of their inhalation.

INTRODUCTION

A DECADE has passed since the publication of the Donora report by the Division of Industrial Hygiene of the U.S. Public Health Service. This report provided pause for reflection on the means by which a reducing-type smog was able to produce such devastating effects on health. At the same time it provided added impetus for research

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already under way on a different type of smog in Los Angeles. The crucial question the Donora report raised was: " How could the known smog components at the low, estimated concentrations result in so much injury? " Similar questions were raised years before in a similar episode in the Meuse Valley, and before that in the London smog disasters of 1873, and later in 1952. Some of that which is to follow shows the progress that has been made to find an experimental solution to the question raised by these acute smog episodes and was unanswered a decade ago.

GENERAL STATEMENT AND THEORY OF INTERACTION

It is becoming increasingly clear from experimental work with simple mixtures of air pollutants that abnormal and unpredictable responses are common findings from single, short exposures of animals. The responses referred to are synergism, antagonism and tolerance development. Although only relatively few instances have as yet been demonstrated, it is suspected that unpredictable effects of mixtures are most commonly related to substances of high toxic potential. It is important to note in this connection that observations previously made with mixtures administered orally or by inhalation concerned substances which did not possess marked toxicity; in these cases additive effects were the rule; examples of moderate synergism and antagonism were only occasionally observed (POZZANI, 1959; CARPENTER *et al.*, 1959).

PHYSICOCHEMICALLY BASED INTERACTIONS

There are several reasons why mixtures of substances taken into the respiratory tract should behave in a less predictable fashion than when injected or when taken orally. The inhalation route presents a number of additional possibilities of interaction of airborne substances not offered by other routes. In the case of vapor and particulate the basic physiocochemical considerations that appear to govern the final toxicologic outcome are:

(1) The degree of adsorption on or absorption into the particle.
(2) The degree of chemical interaction of the substance with the particulate either directly or catalytically.
(3) The relative rate of desorption of the substance from the particulate into the respiratory tract, or
(4) The toxicity of the new combination, if reaction occurs.

Most importantly, these physicochemical considerations permit an extremely high concentration of toxic vapor to be localized on the pulmonary surfaces by simple desorption from the particulate, or of permitting little or none at all of the toxic agent to reach the tissues through lack of desorption, or finally to present a substance of modified toxicity as a result of chemical combination of the particulate and the vapor.

On the basis of these general physicochemical considerations it may be predicted, for example, as GOETZ (1958) has done, that antagonism of the toxic effect will occur if

(a) chemical or catalytic interaction of the adsorbed substance with the particulate occurs to form a compound less toxic than either of the components, or
(b) if adsorbed, the rate of desorption is inappreciable.

Practical examples of (a) have been known or suspected for many years, notably the reduction (antagonism) of the toxic effects on the lung of welding fumes containing acidic nitrogen oxides if particles of basic iron oxide are present. Similarly LABELLE *et al.* (1955) have recorded that the lethal effects of nitrous fumes are materially reduced in acute exposures of mice when inhaled along with particulates that can react

with the nitrogen oxides. A striking example of (b) has been suggested by STEINER (1944) and FALK and STEINER (1952) by the failure to produce cancer in animals when no desorption of the carcinogen from activated carbon into the tissues was shown to occur, but production of cancer, when adsorbed on soot from which desorption occurred. Similarly, the toxic effects of acrolein were shown by LABELLE *et al.* to be antagonized and the effects of formaldehyde synergized when both were adsorbed on the same particulates. This may be explained by the theory of GOETZ on the basis that desorption of the higher-molecular weight acrolein proceeds at a very slow rate whereas formaldehyde is rapidly desorbed.

No doubt based on similar physicochemical interactions are the findings by AMDUR (1959) of enhanced effects of sulfur dioxide and other gases and vapors in guinea pigs when inhaled with either liquid or solid particulates such as sulfuric acid mist or NaCl aerosol. Sulfuric acid mist at 8 mg/m³ and 89 p.p.m. SO_2 together produced more marked effect on growth, more injury to lungs, and greater alterations in respiration than predicted from either alone. Likewise, NaCl aerosol of fine particle size (0·04μ diameter) and at about 10 mg/m³ produced an increase in pulmonary resistance with SO_2 at 2 p.p.m. equivalent to that of 70 p.p.m. SO_2 when inhaled alone, thus providing an apparent potentiation of effect. In this connection it is important to note that the potentiation of effects of SO_2 at low concentrations (2·6 p.p.m.) were proportionately greater than at higher. In accordance with the theory, presumably SO_2 adsorbed on the NaCl aerosol not only carried greater amounts of SO_2 to the deeper portions of the respiratory tract but also enhanced localized concentrations about the aerosol particles. Difficult to explain by the theory, however, is the slightly lesser than normal response when a 2·5μ diameter NaCl aerosol was used; sizes of this magnitude are considered to be in the inhalable range. Moreover, it is important, we believe, to note that the measurement of pulmonary resistance used in this instance is not a measurement of toxicity in the usual sense, such as was the case for the sulfur dioxide–sulfuric acid system, but rather a measure of a normal response mediated by a reflex mechanism of the nervous system.

Enhanced pulmonary airway resistance was also observed with formaldehyde vapors but not with acetic or formic acid in the presence of NaCl aerosol over that from either alone, and the effect persisted, results again in agreement with the interaction theory. Both substances, sulfur dioxide and formaldehyde, which showed potentiated effects are capable of oxidation to substances with greater physiologic response; acetic and formic acids are not.

These findings of AMDUR would seem to provide a basis for an explanation of the abnormal effects seen in the acute smog episodes of Donora, the Meuse Valley and London. The increased resistance to breathing in individuals already having cardiorespiratory difficulties, further enhances the difficulty of obtaining needed O_2. Moreover, this resistance slows down gaseous exchange in the lungs leading to increased accumulation of CO_2. The production of an acidotic condition superimposed on a restricted O_2 intake in pulmonary cripples goes far to explain the effects seen in previous acute episodes.

PHYSIOLOGICALLY BASED INTERACTIONS

The above has dealt briefly with the toxicologic potential derived from the inhalation of a two-phase system of particulate and gaseous air pollutants, and has outlined a

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theoretic basis for toxic effects that departed from those predicted on a purely additive basis. Whereas the theory has helped explain a number of the observed findings in this area, other mechanisms must be invoked to explain the toxicologic interactions observed from the inhalation of single-phase mixtures of gaseous air pollutants when synergism, antagonism or tolerance has been demonstrated.

So little research attention has been given the toxic effects resulting from inhaling mixtures of air pollutants that only general concepts and not precise mechanisms have been developed to explain the abnormal responses of tolerance or synergism. A general explanation of abnormal responses from mixtures of substances entering the body by routes other than inhalation has been developed by VELDSTRA (1956). The explanation is based on a " sites of loss " hypothesis which involves the concept that any substance which interferes with the normal metabolic process of the body to rid itself of the toxic agent will result in an abnormal response. Recently, MURPHY and DUBOIS (1957) have revealed a mechanism to account for the synergistic effect of malathion and EPN which consists of the blocking by malathion of the hydrolytic cleavage of EPN (site of loss). GADDUM (1956) has given mathematic expression to the theory of antagonism if equilibrium is attained by the reactants. None of the mechanisms so far advanced for potentiating drug mixtures would appear to apply to the abnormal effect of inhaled mixtures that are presently being discussed. The physiologic mechanisms involved appear to be far more diverse and complex than those thus far included either in the above mentioned enzymatic blockage, or included in the physicochemical theory, and thus far have defied definition.

EXPERIMENTAL WORK ON MIXTURES OF OXIDANT SMOG COMPONENTS

We have learned in recent years that low concentrations of ozone and other respiratory oxidants may cause serious injury (STOKINGER *et al.*, 1957). Here also a question has arisen. If, as we have repeatedly shown, ozone is so toxic, why have no effects been discernible among the population in Los Angeles, where ozone on many alerts has exceeded 0·5 p.p.m., a level considered to be potentially injurious? The following summarizes results of research that would appear to provide an answer, at least in part, to this question.

TOLERANCE TO ACUTE EFFECTS OF AIR POLLUTANTS

One of the most outstanding and unusual developments thus far of our air pollution studies has been the demonstration of the development of tolerance* to the injurious effects of subsequent acute exposures. This tolerance first demonstrated by STOKINGER *et al.* (1956) with ozone in rats, later confirmed and extended in mice by MATZEN (1957) and in rabbits by SCHEEL *et al.* (1958), is remarkable in that it is induced by exposures of low concentrations (0·3 p.p.m. in mice) of short duration (a few hours). The degree of tolerance afforded is proportional to the O_3 concentration and the time of exposure. Protection from the acute effects of a second exposure may be demonstrated as early as 20 hr in mice and is still demonstrable after 102 days after inhalation exposure to 1 or 2 p.p.m. ozone (MATZEN, 1957). Thus O_3 tolerance has the quality of remarkable

* Definition of tolerance: Tolerance as used here is defined as an increased capacity of the host to resist the effects of subsequent acute exposures to the same agent or different agents (cross-tolerance). Thus, tolerance has the quality of persistence for varying periods of time depending upon the agent and the degree of development of the tolerance. This differentiates tolerance from antagonism which may result from the simultaneous and nonpersistent interaction of two or more agents in the body.

TABLE 1. TOLERANCE TO ACUTE LETHAL EFFECTS OF OZONE
4-hr Exposures—Mice

Ozone pre-exposure concentration (p.p.m.)	Ozone challenge concentration (p.p.m.)	Mortality				Per cent protected
		Pre-exposed		Untreated		
		No. dead / No. exposed	Lung water content %	No. dead	Lung water content %	
2·4	19·2	0/5	82·6	5/5	91·5	100
1·5	8·8	0/4	80·7	5/5	87·2	100
1·0	9·0	0/5	78·4	4/5	86·6	100
0·3	8·9	2/4	86·9	4/5	88·4	30

speed of development and marked duration originating from a single brief exposure; no other substance has yet been demonstrated to possess such a capacity.

Table 1 shows that mice can be protected against multilethal doses of O_3 (19·2 p.p.m. for 4 hr) from a single, 4-hr exposure of O_3 at 2 p.p.m. Ozone concentrations much above 2·4 p.p.m. cause some pulmonary edema which requires a few days recovery period before the challenging dose is administered in order to demonstrate tolerance, but mice subjected to concentrations below 2 p.p.m. can be challenged 18 hr later with uniformly demonstrable protection. It is also seen in Table 1 that a concentration of 0·3 p.p.m. will afford protection for some of the mice (partial protection). In all instances the water content of the lung was less in the ozone-pretreated mice than in the untreated and was proportional in each case to the degree of protection afforded when the magnitude of the challenging dose is taken into consideration. The reduction in edema formation in the lung of the tolerant animals was confirmed by histologic examination. It thus appears that the mechanism responsible for the development of pulmonary edema was blocked. It is important to mention, however, that this tolerance had no effect on the labored breathing pattern imposed by inhalation of ozone, i.e. tolerance does not block all actions of ozone. Moreover, it should be particularly emphasized that the protection against pulmonary injury afforded by this tolerance is against the acute response; the tolerance appears to offer no protection against chronic fibrotic changes from repeated low-grade exposures to ozone (STOKINGER *et al.*, 1957).

The physiologic significance of the ozone tolerance phenomenon is obviously great, particularly from the standpoint of the sporadic peak concentrations occurring in oxidant smog.

CROSS-TOLERANCE AMONG AIR POLLUTANTS

If the demonstration of O_3 tolerance has obvious implications as an inherent protective mechanism against acute smog injury, the demonstration of a " spread " of tolerance to include other air pollutants is of even greater interest. Studies with rats and mice in these laboratories on the capacity of a variety of chemically related and unrelated air pollutants—ozone and four other oxidants—to confer protection on each other have been made on ten combinations. Table 2 shows typical results for

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TABLE 2. CROSS-TOLERANCES AMONG AIR POLLUTANTS TO ACUTE LETHAL EFFECTS
4 or 6-hr Exposures—Mice

Pre-exposure air pollutant		Challenging air pollutant		Mortality				Per cent protection on basis of control deaths
				Retreated		Untreated		
				No. dead		No. dead		
Air pollutant	Concentration (p.p.m.)	Air pollutant	Concentration (p.p.m.)	No. exposed	%	No. exposed	%	
Ozone	1·1	Ketene†	24	0/7	0	7/7	100	100
Ozone	1·0	NO_2	79	0/10	0	7/10	70	100
Ozone*	1·4	H_2O_2	227	14/25	56	22/25	88	36
Ketene†	7·8	Ozone	4·3	0/15	0	1/30	37	100
H_2O_2*	46·2	Ozone	5·6	1/10	10	8/10	80	88
H_2O_2	37	NO_2	77	1/10	10	5/10	50	80
Cumene hydroperoxide‡	100	H_2O_2	226	1/10	10	5/10	50	80
Cumene hydroperoxide‡	100	NO_2	78	5/10	50	5/10	50	0
Cumene hydroperoxide‡	100	O_3	5·6	6/10	60	6/10	60	0
Ozone	1·6	H_2O_2	34·5	0/30	0	13/30	44	100
		Ozone	5·6					

* From SVIRBELY and STOKINGER—unpublished results.
† Ketene exposures were for 10 min, from MENDENHALL and STOKINGER—J. Appl. Physiol., **14**, 923 (1959)
‡ From FLOYD and STOKINGER, *A.M.A. Arch. Industr. Hlth.* **19**, 209 (1958).

mice only. It is seen that eight of the ten combinations tested conferred protection from lethal exposures ranging from 100 per cent to 36 per cent; ozone and ketene were the most effective in this respect. This capacity of ketene is all the more remarkable when it is noted that the exposure providing the protection was for only 10 min duration and was effective against one of the most potent lung irritants, ozone. Hydrogen peroxide was less effective under the conditions of the tests and cumene peroxide was only demonstrably effective against H_2O_2, not against NO_2 or O_3. Indeed, we were unable to demonstrate a protection of cumene peroxide for itself (presumably because of low tissue permeability and diffusion of this relatively large organic molecule). In this connection also it should be noted here that it was far more difficult to develop a tolerance in rodents to NO_2 than to other air pollutants tested; repeated daily exposures for a total of 22 hr to concentrations of 10 p.p.m. NO_2 (1/8 LC_{50}) resulted in no demonstrable tolerance; only by resorting to a high level (32 p.p.m.), single 4-hr exposure was it possible to demonstrate a tolerance in mice to subsequent lethal exposures (mortality: 0/10 pre-exposed vs. 7/10 not pre-exposed to NO_2).

Perhaps one of the more important results given in Table 2 is the last, in which it is shown that a single oxidant (O_3) not only may protect against another but against a mixture of two oxidants, in this case O_3 and H_2O_2, not a mixture with ordinary additive effects, but one with demonstrated synergistic effects (see section on synergistic effects).

Thus, although not all possible permutations and combinations of the five oxidant air pollutants have been tested, we believe sufficient work has been done to provide an indication of a widespread inherent protection from acute response that may result from the inhalation of a single oxidant air pollutant. Further, whatever the mechanism, the demonstrated cross-tolerances indicate a mechanism basic to the oxidant-type air pollutants.

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The mechanism by which this O_3 tolerance develops is at present elusive. Tempting as the idea of an immune mechanism is, this appears to be ruled out on the basis of experiments performed by SCHEEL in these laboratories; mice treated with 6-mercaptopurine to complete inhibition of protein synthesis, which precludes antibody formation (SCHWARZ *et al.*, 1958), still were capable of developing a tolerance to O_3, an occurrence which would seem impossible if immune reactions were the sole mechanism involved. On the other hand, the acute response from O_3, of pulmonary edema and hemorrhage, was minimized in mice given a series of injections of ozonized egg albumin (SCHEEL), a response resembling in type, but not in degree, that possessed by the O_3-tolerant animal. A definite difference in activity of the magnesium-activated fraction of lung alkaline phosphatase has been shown by MOUNTAIN in our laboratories between O_3-tolerant and O_3-susceptible animals, indicating tolerance may involve enzyme adaptation (SCHEEL *et al.*, 1958).

TOLERANCE TO RESPIRATORY OXIDANTS BY OIL MISTS

A significant, but as yet unexplained, protection against the acute effects of the air pollutants, nitrogen dioxide and ozone, following exposure to oil mists has been demonstrated in these laboratories. An unusual aspect was that the protection was not maximal until the day following the exposure to the oil mist. Table 3 reveals that whereas mice showed significant protection from an otherwise lethal exposure of NO_2

TABLE 3. OIL MIST PROTECTION OF ANIMALS FROM ACUTE LETHAL EFFECTS OF OZONE AND NITROGEN DIOXIDE
4-hr Challenging exposure—Mist particle size, 0·5–1·5μ diameter

Conditions of exposure	Oil mist concentration (p.p.m.)*	Respiratory oxidant concentration (p.p.m.)	Mortality				Per cent protection on basis of control deaths
			Pre-exposed		Untreated		
			No. dead / No. exposed	%	No. dead / No. exposed	%	
Min. oil mist, 6 hr 18 hr later NO_2, mice	12	77	0/20	0	11/20	55	100
Min. oil mist, 6 hr 18 hr later, O_3, mice	12	6·8	21/99	21	31/45	69	70
Min. oil mist, 6 hr 18 hr later, O_3, rats	12	8	4/6	66	6/6	100	33
Motor oil mist, 6 hr 18 hr later, O_3, mice	9	7	13/20	65	5/6	85	23
Min. oil mist, 6 hr followed by O_3, mice	33	6	14/80	18	5/10	50	64
Simultaneous min. oil mist and O_3, mice	33	7	41/55	75	14/20	70	–7
Min. oil mist, 6 hr 9 days later, NO_2, mice	12	82	4/10	40	7/10	70	43

* Calculated from values determined as mg/m³ using molecular weight of oil as 200.

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or O_3 when 18 hr elapsed between the exposure to the oil and oxidant (rows 1 and 2), no protection by the oil was demonstrable when the mice were exposed simultaneously to oil and oxidant (row 6); indeed, simultaneous exposure slightly worsened the effect of the oxidant synergism from (physicochemical interaction?). Measurable protection was demonstrable, however, when the agents were administered sequentially (row 5). Table 3 also shows a number of other characteristics of the protection afforded by oil mists. Under the conditions thus far tested,

(1) the oil provided better protection against NO_2 than O_3 (rows 1 and 2),
(2) mice were protected to a significantly greater extent than rats (rows 2 and 3),
(3) mineral oil protects to a significantly greater extent than motor oil (rows 3 and 4), and
(4) significant protection from a single oil exposure persists for at least 9 days (row 7).

This last finding, coupled with the required latent period for development, classifies this response as a tolerance phenomenon, not antagonism.

We are not prepared at this time to present the mechanism by which this tolerance develops. From the nature of the above described effects, the best hypothesis would appear to consist of a hypersecretion of the phagocytic cells or those lining the respiratory tract with the liberation of protective substances.

CROSS-TOLERANCE TO RESPIRATORY OXIDANTS BY ANTU

A tolerance to the acute lethal effects of ozone and NO_2 has been demonstrated in mice and rats by the rat poison, ANTU (alphanaphthylthiourea) by FAIRCHILD *et al.* (1959). Mice given a series of three intraperitoneal injections of ANTU (10 mg/kg on alternate days) were completely protected from lethal effects when challenged the following day with a single, 4-hr exposure of ozone (5·8 p.p.m. for 4 hr) that killed 80 per cent of the unprotected mice; rats challenged with 128 p.p.m. NO_2 18 days after a single, 8 mg/kg dose of ANTU likewise were protected.

Although the mechanism of the tolerance has not been precisely determined, it would appear to resemble the tolerance produced by ozone for the following reasons:

(1) Like ozone, ANTU has been demonstrated to develop a marked tolerance in rats (RICHTER, 1945).
(2) Like ozone, ANTU produces a pulmonary edema in rats.

The cross-tolerance between ANTU and oxidant indicates that the basic mechanisms involved may be similar. Moreover, the antagonism demonstrated by sulfur compounds for these respiratory air pollutants, presented in the following section, points to the involvement of sulfur compounds; ANTU action presumably involves interaction with tissue SH compounds.

EXPERIMENTAL DEMONSTRATION OF SYNERGISM AMONG AIR POLLUTANTS

The possibility of abnormally great responses from the inhalation of mixtures of air pollutants has always been a matter of concern to those involved with the health of working populations, but relatively few bona fide examples of this phenomenon have been demonstrated throughout the years. VON OETTINGEN (1944) has summarized a number of purported examples involving enhanced responses of carbon monoxide with hydrogen cyanide, of carbon monoxide with nitrogen oxide, and carbon mon-

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oxide with hydrogen sulfide. STOKINGER *et al.* (1950) showed that exposures to hydrogen fluoride enhanced the toxicity of beryllium sulfate inhaled by animals. DAUTREBANDE *et al.* (1951) had drawn attention in 1951 to the enhanced effect of particulate matter, sodium chloride and silica, on eye irritation produced by simultaneous exposure to volatile irritants, such as sulfur dioxide, formaldehyde and nitric acid vapor, and pointed to the importance of particle size in connection with effects from air pollutant exposures. LABELLE *et al.* (1955) showed not only synergistic but also antagonistic effects of combinations of these particulates separately administered with formaldehyde, acrolein, and nitric acid vapor. AMDUR's work (1959) showing potentiated effects with sulfur dioxide and particulates has been previously mentioned. It should be noted that all of these studies since 1950 have dealt with abnormal effects of combinations of vapors and particulates. We would like to summarize here a significant instance of synergism not involving particulate interaction but the interaction of two vapors, ozone and hydrogen peroxide, reported by SVIRBELY and STOKINGER (1957).

Table 4 shows that hydrogen peroxide when inhaled at concentrations above 1·5 p.p.m. with acutely noninjurious concentrations of ozone (ca. 1 p.p.m.) was lethal for some of the mice, although more than 200 p.p.m. H_2O_2 alone are required to produce

TABLE 4. SYNERGISTIC EFFECT OF OZONE-HYDROGEN PEROXDE MIXTURES COMPARED WITH EACH SUBSTANCE ALONE
4-hr Exposures—Mice

Average chamber concentration (p.p.m.)		Mortality Number dead / Number exposed
H_2O_2	O_3	
Controls—Exposure to H_2O_2 or O_3		
227	—	9/10
16	—	0/10
—	8	8/10
—	1·1	0/10
Exposure to mixture of H_2O_2 and O_3		
16	0·9	3/10
7·8	0·96	2/10
3·3	1·0	3/10
1·5	0·92	0/10

death in this species and 1 p.p.m. ozone can be tolerated for a lifetime of daily 6-hr exposures by mice (STOKINGER *et al.*, 1957). Synergism of the combination of these two agents was likewise demonstrated in rats which succumbed to exposures of mixtures containing 1 p.p.m. ozone and all concentrations of H_2O_2 above 3·3 p.p.m. (not shown in table). This represents a remarkable case of synergism involving two gaseous air pollutants whose mechanism is not dependent on physicochemical interaction but is presumably mediated by a physiologic process.

The mechanism by which this synergistic action occurs is unknown. However, both H_2O_2 and ozone are respiratory irritants and oxidants; both are capable of denaturing protein (SCHEEL *et al.*, 1958; BLUMENTHAL, 1936). Presumably the similar, but not identical, action of H_2O_2 reinforces the action of O_3, producing an exalted effect.

ANTAGONISM OF SULFUR COMPOUNDS FOR OXIDANT AIR POLLUTANTS

A marked antagonism for the acute lethal effects of ozone and NO_2 has been demonstrated not only for the inorganic air pollutant, hydrogen sulfide, but also for hydrogen polysulfide and a number of organic thiols and disulfides derived from petroleum (FAIRCHILD *et al.*, 1959). Organic sulfides and the ring sulfide compound, thiophene, were not found to be antagonists of these air pollutants.

TABLE 5. EFFECT OF SULFUR COMPOUNDS ON THE TOXICITY OF NITROGEN DIOXIDE AND OZONE FOR MICE

Mortality at 24 and 72 hr is indicated by deaths/number of mice tested

Sulfur compound	Average concentration (p.p.m.)	Oxidant average concentration		Mortality			
				S-Treated		Oxidant alone	
		NO_2	O_3	24 hr	72 hr	24 hr	72 hr
Hexanethiol	145	78	—	0/20	1/20	10/20	11/20
	115	—	4·1	1/20	2/20	10/20	10/20
Methanethiol	65	—	4·8	2/15	2/15	9/15	9/15
Dimethyl disulfide	45	83	—	5/20	5/20	10/20	11/20
	21 mg/kg*	80	—	4/20	4/20	11/20	13/20
	21 mg/kg*	—	4·6	2/20	2/20	10/20	12/20
Hydrogen polysulfide	20 mg/kg*	105	—	8/25	8/25	16/25	18/25
Benzenethiol	14	76	—	1/20	1/20	10/20	10/20
	9	—	6·1	1/20	3/20	11/20	12/20
Hydrogen sulfide†	11	—	4·9	7/35	7/35	17/35	18/35
	1·5	82	—	1/20	2/20	10/20	10/20

* Administered by intraperitoneal injection.
† An aged technical grade.

Table 5 shows the nature of the sulfur compounds that proved antagonistic and the degree to which they were effective against either O_3 or NO_2. The antagonism was demonstrable upon exposure of mice and rats to a mixture of a sulfur compound and the respiratory oxidant. It is seen that hydrogen sulfide of an aged technical grade and presumably containing some polysulfide provided the best protection; 1 mol hydrogen sulfide was capable of protecting animals against 55 mols of NO_2, but aromatic as well as aliphatic thiols provided good protection. The sulfur compounds were more effective antagonists against NO_2 than against ozone. Proof that the mechanism by which protection is afforded is physiologic and not chemical is the protection afforded by injection of certain of the agents shown in Table 5.

The precise mechanism by which the sulfur antagonists act is not completely clear

but apparently the functional unit is –SH and/or –SS, but not –S–; dimethyl sulfide and thiophene were ineffective. Significantly, –SH and –SS– are characteristic of compounds conferring protection against ionizing radiation (FAIRCHILD *et al.*, 1959); for optimal protection, however, an amino group separated by not more than three carbon atoms from the S is required. Against O_3 and NO_2, on the other hand, amino–sulfur compounds provided less than optimal protection. MEG (2-mercaptoethylguanidine-HBr), highly protective against irradiation effects at 200 mg/kg, gave only modest protection against 80 p.p.m. NO_2 (mortality: 8/20 protected, vs. 12/20 NO_2 alone). Thus, similarity, but not identity of action in protective compounds, favors strongly the view that the mechanism of action of the oxidants O_3 and NO_2 mimics that of X-irradiation.

EVIDENCE FOR THE RADIOMETRIC EFFECTS OF OZONE AND ITS SIGNIFICANCE IN AIR POLLUTION

The striking similarity in physiologic antagonism of sulfur compounds for the respiratory oxidants O_3 and NO_2 and radioprotective sulfur compounds just discussed brings into sharp focus a biologic property of these air pollutants that has been unduly disregarded. If evidence can be adduced that these air pollutants mimic the effects of ionizing radiation in the body, then (1) clearer understanding of their biologic activity is directly apparent and (2) a more intelligent pattern of study of their effects is immediately available from the vast background of information on radiation. It is important, therefore, to set forth such evidence as is now known.

(1) The *chemical* evidence that O_3 has free-radical potential and indeed is a biradical containing two unpaired electrons is probably the best evidence for ozone's radiomimetic potential. All O_3 reactions that have been investigated thus far are free-radical reactions. Free radicals are considered to be the chemical mediators in radiation damage to tissue. O_3 produces the same type of free radicals as radiation generates in the aqueous medium of the body. NO_2 containing an impaired electron is one of the few stable free radicals commonly encountered.

(2) In the area of *plant pathology*, O_3 has been shown to produce chromosomal aberrations in *Vicia faba* similar to those of X-irradiation; moreover, the effects of O_3 find X-rays were additive (FETNER, 1958).

(3) *Physiologic alterations* in the form of a defect in oxygen liberation from oxyhemoglobin HbO have been reported by BRINKMAN and LAMBERTS (1958) who have offered this as evidence for the role of "O_3 as a possible radiomimetic gas." Inhalation of 1 p.p.m. O_3 for 10 min by human subjects or u.v. irradiation alike interfered with the dissociation of HbO in the skin of the finger.

(4) In the field of toxicology the increased rate of development and number of lung adenomas in a lung-tumor susceptible strain of mice when exposed daily to 1 p.p.m. O_3 is taken as pertinent evidence of ozone's radiomimetic action.

(5) Aging effects, similar to those seen characteristically from chronic low-level irradiation, developed in animals chronically exposed to low O_3 levels. Like X-irradiation, the effects were cumulative and were produced alike from repeated daily 6-hr exposures to 1 p.p.m. O_3 for 1 year, or from an equivalent dosage of peak concentrations of from 15 to 45 p.p.m. for 1 hr weekly for 1 year.

(6) The finding that agents of similar chemical structure containing –SH and –SS– groups are mutually protective against effects of O_3, NO_2 or ionizing radiation is strong

circumstantial evidence that the basic mechanisms of action of the respiratory oxidants and radiation are similar.

This realization of the radiomimetic character of certain of the oxidant air pollutants throws new light on their toxicologic potentialities and makes more readily understandable the tumorigenic capacity of ozonized gasolines shown by KOTIN *et al.* (1958).

SUMMARY AND CONCLUSIONS

Four distinct types of toxicologic response resulting from the interaction of mixtures of typical air pollutants have been demonstrated—a protective tolerance and cross-tolerance, synergism and antagonism. Under the conditions of the demonstrations, these responses apply to the acute, toxic phase.

Ozone and ketene produced from a single, brief exposure an immediate, marked protection of varying duration in animals against subsequent, otherwise lethal exposures. Cross-protection was demonstrated likewise for O_3 and ketene against a number of other air pollutants of the oxidizing type not necessarily related in chemical structure. Oil mists, both motor and mineral, provided a tolerance to ozone and nitrogen dioxide; ANTU similarly protected animals.

A significant antagonism resulting in the protection of animals from the lethal effects of ozone and nitrogen dioxide has been demonstrated for a number of sulfur compounds derived from petroleum when inhaled in admixture. Both inorganic and organic sulfur compounds were effective antagonists provided they contained the –SH or –SS– grouping; organic sulfides were not antagonistic.

An instance of pronounced synergism in rodents was found when a mixture of ozone and hydrogen peroxide was inhaled; levels of H_2O_2 above 1·5 p.p.m. with 1 p.p.m. O_3 were lethal to some animals, a response obtained with H_2O_2 only at levels around 200 p.p.m.

The mechanisms which govern these abnormal toxicologic responses of single-phase mixtures of air pollutants are largely unknown –H_2O_2–O_3 synergism and tolerance and cross-tolerance phenomena among certain respiratory oxidants. In the latter instances, however, some experimental evidence points to the development of adaptive enzymes as playing at least a partial role. In the toxicologic antagonism of sulfur compounds for O_3 and NO_2, it is believed, by analogy with the action of radioprotective compounds, that the sulfur compounds act as free-radical traps. In this connection, six experimental pieces of evidence are presented for the radiomimetic nature of O_3.

In the abnormal toxicologic responses from biphasic mixtures of air pollutants the physicochemical theory of GOETZ provides an explanation for many of the unusual results obtained with such systems.

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PHOTOCHEMICAL AEROSOL FORMATION IN SULFUR DIOXIDE-HYDROCARBON SYSTEMS*

N. A. RENZETTI† and GEORGE J. DOYLE‡

(*Received* 8 *October* 1959)

Abstract—We have conducted a series of photochemical experiments in a 50-l. stirred-flow reactor to study aerosol formation from different hydrocarbons in the presence of nitrogen oxides and sulfur dioxide.

Irradiation by simulated sunlight of trace concentrations (p.p.m.) of the reactants, in some cases, yielded particles in the size regime 0·1–0·3 μ diameter, which by scattering of light are important to visibility in the atmosphere. A large number of experiments with 3 p.p.m. of various hydrocarbons, 1 p.p.m. nitrogen oxides, and 0·1 to 0·5 p.p.m. SO_2 indicated that the olefinic hydrocarbons were the only important aerosol formers in contrast to the paraffinic and aromatic hydrocarbons. It was observed that the photolysis of sulfur dioxide proceeds at the rate of 0·4 per cent per minute which is considerably above that observed by JOHNSTONE and GERHARD (1955). The high sulfate content of the particulate matter and low gaseous sulfur dioxide concentrations observed in the Los Angeles smog are consistent with the findings of this laboratory program.

INTRODUCTION

EXPERIMENTAL studies of the smog problem have been concentrated on elucidation of the process of photo-oxidation occurring in urban atmospheres containing traces of hydrocarbon and nitrogen oxides. Relatively little effort has been devoted to the study of aerosol formation, pending the development of some understanding of the chemistry involved. The formation of aerosols (SCHUCK, 1958a; DOYLE, 1958), and a possibly important role of sulfur dioxide in aerosol formation have been demonstrated in irradiated dilute mixtures of auto exhaust and air (SCHUCK, 1958b; STEPHENS, 1958; RENZETTI, 1959). HAAGEN-SMIT and co-workers (1952, 1956) have demonstrated aerosol formation from irradiated mixtures of air and concentrations of hydrocarbons and oxides of nitrogen around a few parts per million by volume. In this work the cyclo-olefins were found to be the most potent aerosol formers.

The present study is part of a program being conducted by Stanford Research Institute under the sponsorship of the Air Pollution Foundation. This program is aimed at elucidating the chemistry of photo-oxidation, the mechanism of aerosol formation, and the properties of aerosols so produced. The work reported here covers a preliminary study of the important parameters governing aerosol formation and a cursory survey of the potential of hydrocarbon types for aerosol formation.

EXPERIMENTAL

Apparatus

The photo-oxidations were carried out in a stirred-flow reactor consisting of a 50-l. round bottom Pyrex flask fitted with an all-glass paddle-wheel recirculating

* Presented at the International Clean Air Conference, London, 20–24 October, 1959.
† Air Pollution Foundation.
‡ Stanford Research Institute.

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blower (30 l/min) to draw air from the bottom of the flask and discharge it through the flask neck. Air for the reaction mixture was drawn by means of a diaphragm pump from a manifold carrying purified air for a large irradiation chamber (SCHUCK, 1957, 1958b). The air stream was forced through a bed of activated alumina (Laboratory Lectrodryer) and split into two metered streams. One stream was passed countercurrent to a dropwise stream of water through a bed of glass Raschig rings. Near-saturation of this air stream was achieved by adjusting the electric current through glass heating tape wrapped around the downstream end of the bed until the temperature at the upstream end was approximately equal to the ambient. This saturated stream was then mixed with the other metered stream (thus obtaining an air stream of known relative humidity), preheated and passed through a 5-in. by 1·5-in. bed of platinized alumina at 600°C, cooled in copper tubing, metered, and discharged into a mixer.

The other components of the reaction mixture were fed to the mixer through glass capillary tubing and sensitive float-type flow meters from pressurized stainless steel tanks containing reactant gases greatly diluted with prepurified nitrogen. The mixer consisted of a 125-ml flask sealed on to a float-type flow meter. The main air stream was entered tangentially to cause a swirling motion in the flask over the capillary jets through which all of the minor components, except nitric oxide entered the mixer. Dilute nitric oxide was introduced through a capillary jet in the throat of the flow meter to shorten its mixing time and thus to avoid its undue oxidation to nitrogen dioxide. The major mixing action for this component took place in the annulus around the glass float of the flow meter. The stream from the mixer then passed through an aerosol filter consisting of three pads of fired MSA 1106 glass mat (YAFFE, 1956) and into the reactor at the throat of the recirculating blower.

The effluent stream from the reactor was taken from the recirculating stream just after it came from the bottom of the reactor. The effluent stream was then fed to various instruments, including an aerosol counter photometer (O'KONSKI, 1954, 1955, 1956) for measurement of light-scattering properties, a nuclei counter of the Aitken type (VONNEGUT, 1949) and a continuous analyzer based on colorimetric method for analysis of sulfur dioxide (HELWIG, 1958; STEIGMAN, 1942; URONE, 1951; PAULUS, 1954; ATKINS, 1950; WEST, 1956). Occasionally, a similar type of recorder was used for analysis of nitrogen (THOMAS, 1956).

Light-scattering measurements were always carried out using diluting and sheath air streams of essentially the same humidity as the reactor effluent to avoid hydration or dehydration of the aerosol particles. This was done by using a closed-circuit counter photometer flow control system (O'KONSKI, 1956) where leakage was held to a negligible rate. The system was vented at a known flow rate so that samples could be taken at a known rate. Before each experiment the control system was equilibrated by allowing air of controlled humidity to flow from the reactor through the system at several liters per minute for about an hour. This same relative humidity was then used in the subsequent experiment.

Irradiation was by means of four General Electric H 400-E1 medium-pressure mercury arc lamps placed symmetrically about the 50-l. reactor. The radiation was filtered by the Pyrex lamp envelopes and the walls of the reactor. The intensity within the flask was augmented by enclosing the flask with aluminium foil having four windows 6 in. by 6 in. The resulting intensity distribution within the reactor

had been previously studied and found to be relatively uniform (FORD, 1959).

Previously, an intensity of $9{\cdot}2 \times 10^{15}$ quanta sec^{-1} cm^{-2} had been measured within the reactor with water-cooled filters (Corning specification 7-60) in the light path to isolate the 366mμ line (FORD, 1957). Using General Electric Company's data for the spectral power distribution of H 400-E1 lamps and the transmittance of Corning filters plus the transmittance of water made it possible to obtain a figure for the geometric efficiency of the irradiation system of $2{\cdot}78 \times 10^{-5}$ cm^{-2}. Because of the approximate nature of some of the basic data it was not considered worth-while to take into full account in the calculation the reflection phenomena at interfaces of the composite filter. However, in the absence of actual measurement of spectral distribution within the reactor this calculated efficiency yields approximate values of the spectral distribution within the reactor, using G.E.'s spectral power distribution data as a base of calculation and the expression

$$P_\lambda \times \lambda \times 5{\cdot}04 \times 10^{16} \times 4 \times 2{\cdot}78 \times 10^{-5} \times T_\lambda \text{ quanta } sec^{-1}\ cm^{-2}\ (10m\mu)^{-1}$$

where P_λ = power spectral distribution in watts, T_λ = reactor wall transmittance, and λ = wavelength in millimicrons. The result is shown in Fig. 1 and is compared with

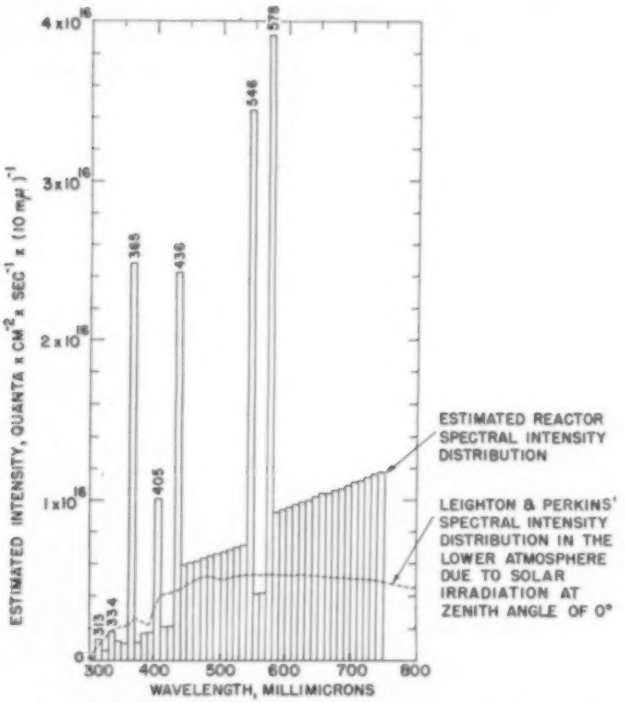

FIG. 1. Estimated spectral intensities within the reactor and in sunlight.

LEIGHTON and PERKINS' values of the corresponding quantities for sunlight under representative conditions at a solar zenith angle of 0° (LEIGHTON, 1956, p. 129). The result may be expected to be least accurate near 300mμ.

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Materials

Air purified in the above-described purification train was examined by means of a long-path infrared spectrophotometer and analyzed by a NO–NO_2 recording colorimeter. The pure air contained less carbon dioxide than did the ambient air (probably because of adsorption by the activated alumina) and less than two parts per hundred million of nitrogen oxides. No significant amount of impurities, such as hydrocarbons, were detected—that is, less than 0·2 p.p.m. were present. Blank runs using a SO_2 colorimeter recorder did not indicate the presence of sulfur dioxide—that is, less than 0·01 p.p.m. were present. Sulfur dioxide is probably removed by adsorption in the drying tower and by oxidation over the hot platinum catalyst.

The nitric oxide used was Matheson C.P. grade. The hydrocarbons were mainly Phillips Pure Grade or Matheson C.P. grade. In some instances, particularly in the case of aromatic hydrocarbons, C.P. grades of other manufactures were used. Ethyl benzene was taken from a lot which had been purified by distillation in this laboratory. The 1-butyne was taken from an API standard sample ampoule. The prepurified dry nitrogen used to pressurize and dilute the reactants was obtained from Air Reduction Company.

Reactants were stored in stainless steel tanks which had been washed thoroughly with organic solvents, dilute acid, detergent, and distilled water and then had been steamed out. After steaming, the tanks were baked at ca. 150°C, fitted with plugs and valves, and again baked under evacuation at ca. 10^{-5} mm. The latter step was repeated before each refilling of the tanks.

The tanks were filled by means of an all-metal vacuum manifold coupled to a conventional oil diffusion pump. After evacuation, the system was filled with the desired gas to a predetermined static pressure. Prepurified nitrogen was then bled into the system from a high-pressure cylinder until the desired 100 psig final pressure was attained. The necessity of accurately measuring the rate of flow into the reactor usually imposed the condition that these bleeder tanks contain reactants at a concentration around 100 p.p.m. by volume.

Liquid reagents were freed of dissolved gases by several repetitions of the freeze–pump–warm technique before the vapor was allowed to enter the metal vacuum system.

Experimental Data

Photo-oxidation of sulfur dioxide in air of 50 per cent relative humidity. A rough estimate of the small decrease of sulfur dioxide concentration due to photo-oxidation was obtained in several experiments in which only sulfur dioxide and water vapor were present. These data are given in Table 1. The absorption rate of sulfur dioxide in the reactor was estimated to be 0·013 min^{-1} calculated from the data of Fig. 1 and the absorption coefficients found by HALL and BLACET (LEIGHTON, 1956, p. 60). Combination of the average rate of photo-oxidation with this absorption rate gave a quantum yield for sulfur dioxide consumption of about 0·3.

This rate and quantum yield were based on the assumption that the secondary photochemical processes are such that the rate is directly proportional to the sulfur dioxide concentration found by HALL and BLACET (LEIGHTON, 1956, pp. 50–54) under considerably different conditions.

TABLE 1. RATE OF PHOTO-OXIDATION OF SULFUR DIOXIDE IN 50% R.H. AIR

Experiment number	Sulfur dioxide concentration (p.p.m.)			Residence (min)	Rate of photo-oxidation (min^{-1})
	Influent	Effluent	Decrement		
19 AS	0·61	0·52	0·09	27	0·006
8 AS	0·52	0·47	0·05	17	0·006
11 AS	0·28	0·27	0·01	17	0·002
14 AS	0·22	0·20	0·02	27	0·004

Average $(4{\cdot}5 \pm 1{\cdot}2) \times 10^{-3}$ min^{-1} (50% Conf.)

These authors found a considerably smaller quantum yield of 0·036 at 3130Å and 25°C (dry system, $P_{SO_2} = 12{\cdot}7$ mm, $P_{O_2} = 10{\cdot}6$). The sources of the difference are probably the higher total pressure, the much lower concentrations, and the presence of water vapor, combined with probable large errors in estimating absorption rates and the rate of photo-oxidation in the Institute's reactor. If the same quantum yield of 0·3 is assumed for sunlight, then a photo-oxidation rate of 0·004 min^{-1} is obtained for the spectral distribution in the lower atmosphere shown in Fig. 1. This is in sharp contrast with the rate of ca. 2×10^{-5} min^{-1} experimentally found for sunlight by GERHARD and JOHNSTONE (1955). One factor probably contributing to this lack of agreement is the extreme variability of solar intensity in the region of effective sulfur dioxide absorption, 300–340mμ.

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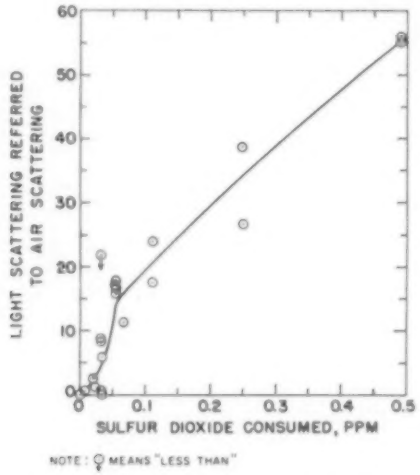

FIG. 2. Light scattering as a function of the amount of sulfur dioxide photo-oxidized in 50 per cent relative humidity air.

Data on light scattering from the reactor effluent from photolyzing mixtures of sulfur dioxide and pure air of 50 per cent relative humidity are summarized in Fig. 2. The ordinate represents the amount of light scattered, from 2 μl of aerosol, corrected for air scattering, divided by the amount scattered by an equal volume of air under the conditions prevailing in the counter photometer cell (O'KONSKI, 1956). The

abcissa represents the amount of sulfur dioxide photo-oxidized to form the aerosol, estimated by use of the experimentally determined $4{\cdot}5 \times 10^{-3}$ min^{-1} rate. These data are given in detail in Table 2.

The shape of the curve in Fig. 2 is probably determined by the variation in response of the counter photometer with average particle size. For sulfur dioxide consumptions greater than about 0·05 p.p.m., the greater amount of aerosol mass is probably contained in particles large enough to give a response approximately proportional to the square of the diameter (O'KONSKI, 1956). In fact, a plot of scattering vs. the 2/3 power of sulfur dioxide consumed is not inconsistent with the hypothesis that approximately the same number of particles of sizes greater than ca. 0·2μ (GUCKER, 1955) are produced when the consumption exceeds 0·05 p.p.m. Apparently, when the consumption is less than this, the diameters lie in the transition region where scattering is going from a " square law " response to a sixth power response. In addition, the particle concentration may be rapidly varying in this region.

TABLE 2. LIGHT-SCATTERING AND SULFUR DIOXIDE CONCENTRATION DATA FOR PHOTO-OXIDATION IN 50% R.H. AIR

Experiment number	Residence time (min)	Sulfur dioxide data (p.p.m.)					Light-scattering data	
		Influent		Effluent	Increment			
		From tank data[a]	Measured[b]		Measured[b]	Calculated	Total referred to air	Count (ml^{-3})
11 A-1	17	0·11	NI	NI	NI	0·01	0·75	NI
11 A-2	17	0·30	NI	NI	NI	0·02	2·58	32
5A-2	17	0·47	NI	NI	NI	0·03	<22	NI
6 A-2	17	0·47	NI	NI	NI	0·03	5·9	184
6 A-4	17	0·47	NI	NI	NI	0·03	9·0	NI
7 A-2	17	0·47	NI	NI	NI	0·03	≳8·7[c]	NI
7 A-4	17	0·47	NI	NI	NI	0·03	≳0·59[c]	NI
7 A-5	17	0·47	NI	NI	NI	0·03	≳0·19[c]	NI
14 AS-1	27	NI	0·22	0·20	0·02	0·02	1·07	NI
17 AS-2	27	0·51	0·63–0·90	0·61	0·02–0·29	0·06	17·9	NI
17 AS-3	27	0·51	0·63–0·90	0·64	<0·00–0·26	0·06	17·4	1080
17 AS-4	27	0·51	0·63–0·90	0·75	<0·00–0·15	0·06	15·9	NI
17 AS-6	27	0·51	0·63–0·90	0·71	<0·00–0·19	0·06	16·9	NI
19 AS	27	NI	0·61	0·52	0·09	0·07	≳11·3[c]	NI
16 AS-5	27	1·02	1·34	1·20	0·14	0·11	≳24[c]	NI
16 AS-6	27	1·02	1·34	0·98	0·36	0·11	17·5	1190
16 AS-2	27	2·27	2·58	2·62	<0·00	0·25	38·7	1730
16 AS-3	27	2·27	2·58	2·40	0·18	0·25	26·7	NI
15 AS-2	27	4·49	3·48	3·81	<0	0·49	56	3990
15 AS-3	27	4·49	3·48	4·18	<0	0·49	55	NI

NI means no information.

[a] These concentrations were calculated from the partial pressure of sulfur dioxide in the stainless steel reagent storage tank and flow rates into the mixer.

[b] Measurements of sulfur dioxide in the reactor stream were occasionally very inaccurate and indefinite because of wall sorption effects and/or malfunction and slow response of the sulfur dioxide recorder. On those occasions when it was thought that the recorder was at fault, greater reliance was placed on the calculated concentrations.

[c] Indicates that the light scattering was varying in a quasi-periodic manner and that the value given is the peak of the variation and that the minimum value is of the same order of magnitude as the peak.

The importance to air pollution of photo-oxidation of minute amounts of sulfur dioxide to sulfuric acid aerosol can be brought out by a simple calculation which shows that the complete conversion of 0·05 p.p.m. of sulfur dioxide to aerosol at 50 per cent relative humidity will result in a mass loading of ca. 460μg/m^3 of ca. 43 per cent solution of sulfuric acid. A loading of this magnitude can lead to a significant reduction of visibility, as supported by the measured light scattering shown in Fig. 2.

The size distribution of particles above the counting threshold of the counter photometer are shown in Fig. 3 for three of the higher influent concentrations of sulfur dioxide. The size scale is in terms of polystyrene spheres used to calibrate the counter. It is obvious that a considerable number of optically significant particles were present and that the number increased with increasing amounts of sulfur dioxide consumed.

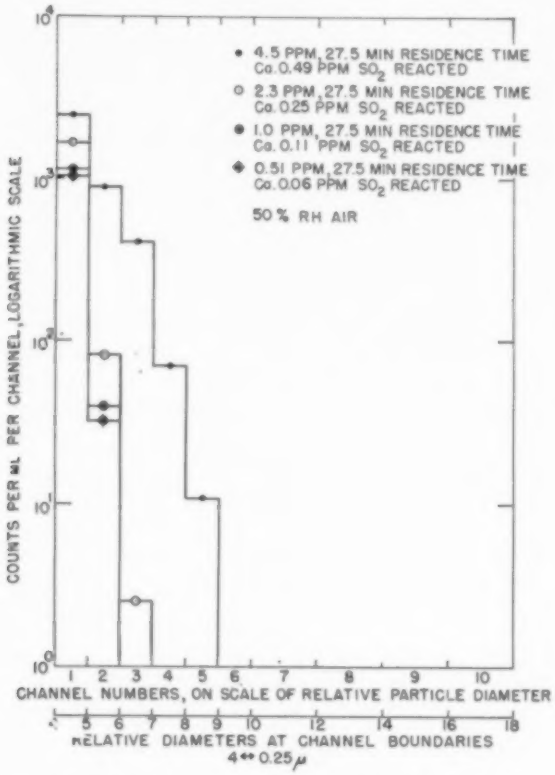
4.5 PPM, 27.5 MIN RESIDENCE TIME
Co. 0.49 PPM SO_2 REACTED
2.3 PPM, 27.5 MIN RESIDENCE TIME
Co. 0.25 PPM SO_2 REACTED
1.0 PPM, 27.5 MIN RESIDENCE TIME
Co. 0.11 PPM SO_2 REACTED
0.51 PPM, 27.5 MIN RESIDENCE TIME
Co. 0.06 PPM SO_2 REACTED
50 % RH AIR
COUNTS PER ml PER CHANNEL, LOGARITHMIC SCALE
CHANNEL NUMBERS, ON SCALE OF RELATIVE PARTICLE DIAMETER
RELATIVE DIAMETERS AT CHANNEL BOUNDARIES
4 ↔ 0.25 μ

FIG. 3. Particle size distributions of aerosols produced by photo-oxidizing sulfur dioxide in 50 per cent relative humidity air.

A separate experiment was carried out in which both light-scattering concentration and condensation nuclei (for water) concentration were followed as a function of time after the light shutters were opened. The result is shown in Fig. 4. A great number of nuclei appeared immediately and then decayed to an intermediate value while the light scattering increased steadily. The steady-state consumption estimated for this

experiment was 0·02 p.p.m., which lies in the transition region of Fig. 2. It is evident that a great many particles of very low light-scattering ability—that is, very small dia-

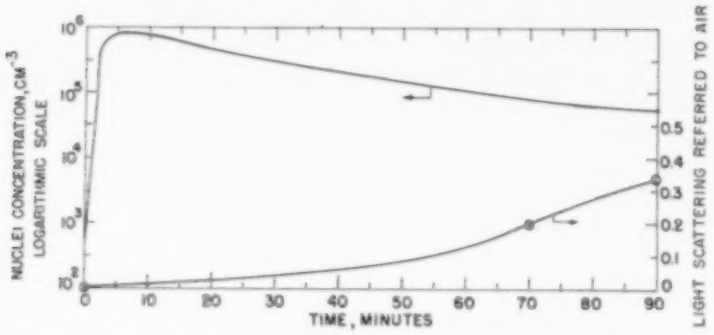

FIG. 4. Variation of nuclei and light scattering with time in effluent from photo-oxidized mixture of 0·24 p.p.m. sulfur dioxide with 50 per cent relative humidity air (residence time 18 min).

meter, were present. Combination of the estimated sulfur dioxide consumption with the nuclei count indicates a sulfuric acid content of $1{\cdot}24 \times 10^{-15}$ g per particle. If the particle is assumed to have a density of 1·34 g/ml and to consist of a 44 per cent solution of sulfuric acid in water, then one obtains $<d^3>^{1/3} \simeq 0{\cdot}16\mu$ in which d = particle diameter. Since this value represents the third moment of the size distribution, the first moment is probably much less than this figure. This suggests that the photo-oxidation of very small amounts of sulfur dioxide can supply ample acidic nuclei for either physical or chemical condensation of other materials present in the atmosphere.

Only one experiment in this series was carried out to determine the effect of water vapor on sulfur dioxide photo-oxidation. The data are given in Table 3. Unfortunately, no measurements of effluent concentrations were made during this sequence of experiments to observe possible effects on the photo-oxidation rate. The effect on light scattering was striking, as Table 3 indicates.

TABLE 3. LIGHT-SCATTERING AND SULFUR DIOXIDE CONCENTRATION DATA SHOWING EFFECT OF RELATIVE HUMIDITY (Influent sulfur dioxide concentration, 0·47 p.p.m.; estimated sulfur dioxide consumption 0·033 p.p.m.; residence time 17 min)

Experiment number	Relative humidity	Light scattering
6 A-2	50	5·9
6 A-3	0	0·73 (and still decreasing)
6 A-4	50	9·0

Photo-oxidation of sulfur dioxide in the separate presence of nitrogen oxides and hydrocarbons

Nitrogen oxides. In one set of experiments nitric oxide (1 p.p.m.) was added to several photo-oxidizing mixtures of SO_2 (0·5 p.p.m.) in 50 per cent R.H. air. There were some indications that the formation of aerosol was hindered by nitric oxide.

However, more experimental work will have to be carried out before a definite conclusion can be reached.

The addition of nitrogen dioxide to irradiated mixtures could enhance the oxidation of sulfur dioxide and increase the resultant light scattering because a rate constant of 3×10^{10} l^2 mole^{-2} sec^{-1} has been reported for the reaction

$$SO_2 + O + M \rightarrow SO_3 + M.$$

Two experiments (0·14 p.p.m. SO_2, 1 p.p.m. NO_2) gave qualitative indication of an effect of this sort.

Hydrocarbons. A few experiments in which butadiene or pentene-1 (3 p.p.m.) was added to photo-oxidizing sulfur dioxide (0·3 p.p.m.) indicated that the addition of these olefins has a strong suppressive effect on the production of light-scattering aerosol. Possibly the olefins interfere with the chemical reactions and/or with the physical process of aerosol formation.

Enhancement of aerosol production and of sulfur dioxide photo-oxidation by co-photo-oxidation of 2-methyl 2-butene with nitric oxide

A fairly extensive investigation was made of the enhancement of aerosol production and of sulfur dioxide photo-oxidation by co-photo-oxidation of 2-methyl 2-butene with nitric oxide. These experiments were carried out at 50 per cent relative humidity, keeping the nitric oxide concentration at 1·0 p.p.m. Residence time, sulfur dioxide concentration and hydrocarbon concentration were varied. The data are given in

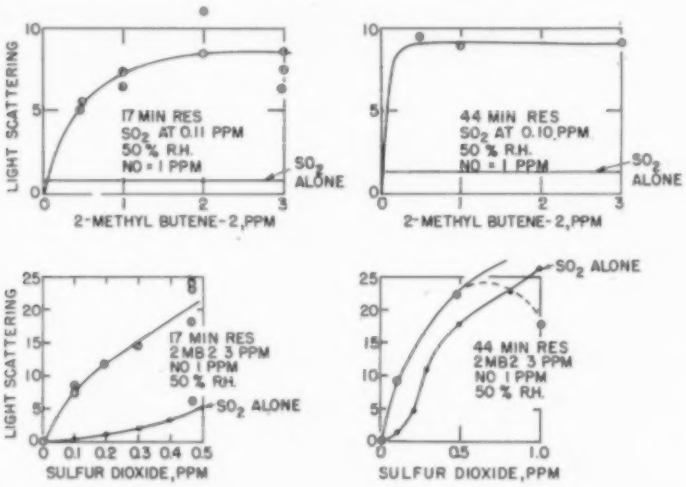

FIG. 5. Some cuts through the dimensional space of the data of Table 7 compared with light scattering in the absence of hydrocarbon and nitric oxide.

Table 4, and some cuts through the data are illustrated in Fig. 5. The light scattering predicted for photo-oxidation of sulfur dioxide alone (see Fig. 2) is also shown in Fig. 5 to bring out the marked enhancement resulting from photo-oxidation of the hydrocarbon. It is interesting to note that as much light scattering can be produced with 0·2 to 0·5 p.p.m. of hydrocarbon as with 0·5 to 3 p.p.m., provided that sufficient residence time is allowed for the reaction (same concentration of nitric oxide and sulfur

dioxide). Increasing amounts of sulfur dioxide led to increasing light scattering. Perhaps this latter effect will saturate due to interference by sulfur dioxide with the hydrocarbon oxidation as indicated in the lower right-hand graph in Fig. 5.

TABLE 4. PHOTOLYSIS OF MIXTURES OF 2-METHYLBUTENE-2 NITRIC OXIDE, AND SULFUR DIOXIDE

Experiment number	Residence (min)	Irradiation	Influent concentration (p.p.m.)			Effluent data		
			SO_2	HC	NO	Light scattering	Particle count (ml^{-1})	SO_2 concentration (p.p.m.)
3 A-3	17	Yes	0·094	2·9	0·96	6·2	242	NI
9 AS-3	17	No	0·11	0·49	0·98	NI	NI	0·11
9 AS-4	17	Yes	0·11	0·49	0·98	NI	NI	0·01
9 A-1	17	Yes	0·11	0·49	0·98	5·6	NI	NI
10 A-1	17	No	0·11	0·49	0·98	0·00	NI	NI
10 A-2	17	Yes	0·11	0·49	0·98	5·2	NI	NI
9 A-2	17	Yes	0·11	0·99	0·98	6·4	NI	NI
10 A-3	17	Yes	0·11	0·99	0·98	7·3	NI	NI
9 A-3	17	Yes	0·11	1·98	0·98	11·1	NI	NI
10 A-4	17	Yes	0·11	1·98	0·98	8·4	NI	NI
9 A-4	17	Yes	0·11	2·9	0·98	7·4	NI	NI
10 A-5	17	Yes	0·11	2·9	0·98	8·7	NI	NI
3 A-4	17	Yes	0·19	2·9	0·96	11·8	590	NI
10 A-6	17	Yes	0·30	2·9	0·98	14·5	NI	NI
2 A-3	17	Yes	0·47	2·9	0·96	6·4	511	NI
3 A-5	17	Yes	0·47	2·9	0·96	18·3	896	NI
7 A-7	17	Yes	0·47	2·9	0·96	24·2	NI	NI
8 A-1	17	No	0·47	2·9	0·96	0·00	NI	NI
8 A-2[a]	17	Yes	0·47	2·9	0·96	23·6	1000~	NI
8 A-3[a]	17	Yes	0·47	2·9	0·96	7·5	358	None
8 AS-3	17	No	0·52	2·9	0·96	NI	NI	0·52
8 AS-4	17	Yes	0·52	2·9	0·96	NI	NI	0·40
12 A-1	44	No	0·10	0·50	1·0	0·00	NI	NI
12 A-2	44	Yes	0·10	0·50	1·0	9·5	NI	NI
12 A-3	44	Yes	0·10	1·0	1·0	8·9	NI	~0·005
12 A-4	44	Yes	0·10	3·0	1·0	9·2	NI	~0·005
2 A-4	44	Yes	0·47	3·0	1·0	22·3	1028	NI
12 A-5	44	Yes	1·0	3·0	1·0	17·8	680	0·4–0·5
2 A-5	84	Yes	0·47	2·9	0·96	≥26·1	1200~	NI
2 A-6	84	No	0·47	2·9	0·96	→0	NI	NI

NI means no information.

[a] Subsequent to experiment 8A-2 the humidifier was bypassed. During experiment 8A-3 the relative humidity was approaching 0·0 per cent.

The increase in light scattering is most marked at the lower sulfur dioxide concentration. This probably results from the afore-mentioned transition in photometer response from diameter to the sixth power to the square of the diameter with increasing diameter which renders the method most sensitive to changes at low sulfur dioxide concentrations. However, the changes are good measures of the optical importance of the particles produced.

The particle count tends to parallel the light scattering in those cases where it was measured. The count per size class rose steeply with decreasing particle size in a manner similar to that observed in distributions in irradiated automobile exhaust (DOYLE, 1958). The background of larger particles observed in the latter case was absent because the reaction mixture was filtered.

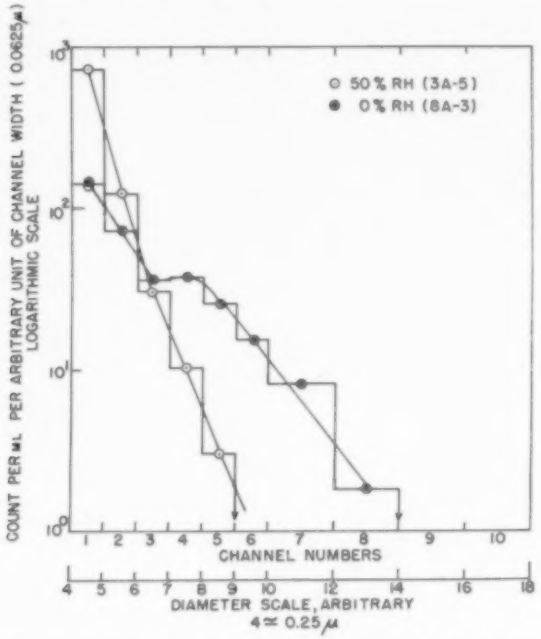
COUNT PER ml PER ARBITRARY UNIT OF CHANNEL WIDTH (0.0625μ)
LOGARITHMIC SCALE
○ 50% RH (3A-5)
● 0% RH (8A-3)
CHANNEL NUMBERS
DIAMETER SCALE, ARBITRARY
4 ∝ 0.25 μ

FIG. 6. Contrasts in counts per milliliter and particle size distribution between aerosols formed by photolysis of 3 p.p.m. 2-methylbutene-2, 1 p.p.m. nitric oxide, and 0·5 p.p.m. sulfur dioxide in dry and in humid air.

Experiment No. 8 A-3 (see Table 4) was a deviation from the experimental plan. The humidity was allowed to decrease, and as it decreased the light scattering decreased and the particle size distribution changed, as shown in Fig. 6. It is evident that humidity has a marked effect, which is currently under investigation.

TABLE 5. DATA SHOWING INCREASED RATE OF CONSUMPTION OF SULFUR DIOXIDE DUE TO PHOTO-OXIDATION OF 2-METHYL 2-BUTENE BY NITRIC OXIDE

Experiment number	Residence time (min)	Influent concentration (p.p.m.)			SO_2 in effluent concentration (p.p.m.)	SO_2 disappearance rate (p.p.m./min)	Calculated photo-oxidation rate (p.p.m./min)	Enhancement ratio
		HC	NO	SO_2				
9 AS-4	17	0·49	0·98	0·11	0·01	0·0059	0·00046	13
8 AS-4	17	2·9	0·96	0·52	0·40	0·0070	0·0022	3·2
12 A-3	44	1·0	1·0	0·10	~0·005	0·0022	0·00038	5·8
12 A-4	44	3·0	1·0	0·10	~0·005	0·0022	0·00038	5·8
12 A-5	44	3·0	1·0	1·0	0·45	0·012?	0·0038	3·2

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Additional data on those Table 4 experiments in which measurements of effluent sulfur dioxide were made are shown in Table 5. Values of the rate of sulfur dioxide disappearance are compared with the rate predicted from the SO_2 photo-oxidation rate (Table 1) to illustrate that the photo-oxidation of the hydrocarbon accelerates the rate of disappearance of sulfur dioxide.

Nuclei in co-photo-oxidizing mixtures of olefin, nitric oxide and sulfur dioxide

An attempt was made to duplicate in a synthetic system the results obtained with irradiation of auto exhaust from olefin and sulfur-containing fuels (SCHUCK, 1958b). For this purpose a mixture of 3 p.p.m. 2,3-dimethyl 2-butene, 1 p.p.m. nitric oxide, and 0·1 p.p.m. sulfur dioxide air was irradiated in the reactor with 50 per cent relative humidity at a residence time of 27 min. Light scattering and nuclei in the effluent were each measured as a function of time. The results are shown in Fig. 7 along with

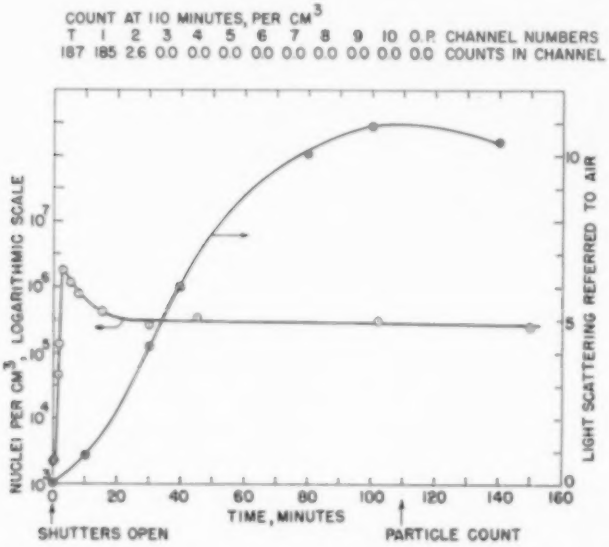
COUNT AT 110 MINUTES, PER CM3
T 1 2 3 4 5 6 7 8 9 10 O.P. CHANNEL NUMBERS
187 185 2.6 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 COUNTS IN CHANNEL
NUCLEI PER CM3, LOGARITHMIC SCALE
LIGHT SCATTERING REFERRED TO AIR
TIME, MINUTES
SHUTTERS OPEN
PARTICLE COUNT

FIG. 7. Nuclei, light-scattering and particle-size distribution data on the effluent from a photo-oxidizing mixture of 3 p.p.m. 2,3-dimethylbutene-2, 1 p.p.m. nitric oxide, and 0·1 p.p.m. sulfur dioxide in 50 per cent relative humidity air (residence time 27·5 min).

the data on a particle count made at steady state. The behavior of the auto exhaust mixture was qualitatively duplicated. However, the steady-state nuclei concentration was an order of magnitude greater, and the particle count was lower, than for auto exhaust. This may be attributed to the considerable differences in estimated concentration (~0·5 p.p.m. sulfur dioxide for the auto exhaust) and to qualitative differences in the kind of hydrocarbon present.

Nuclei concentration in the absence of sulfur dioxide was also measured in the case of mixtures of *cyclo*hexene (3 p.p.m.) and nitric oxide (1 p.p.m.). This is the only one of the hydrocarbons tested (see below) which yielded considerable aerosol in the absence of sulfur dioxide. The results are shown in Fig. 8. The considerable number of nuclei for water condensation appear as a transient peak which then decays towards an apparent steady-state level $\sim 10^4$ cm^{-3}.

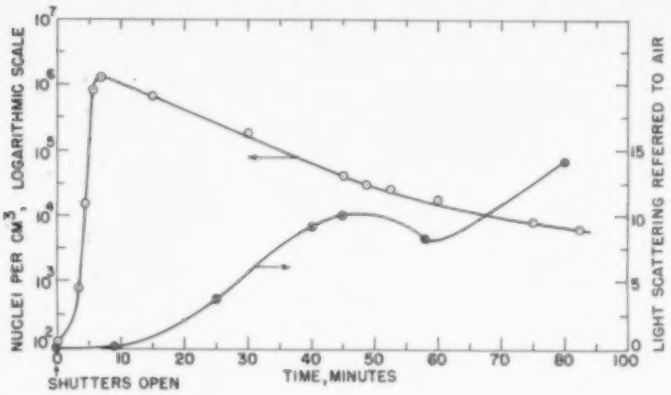

FIG. 8. Nuclei and light-scattering data on the effluent from a photo-oxidizing mixture of 3 p.p.m. *cyclo*hexene and 1 p.p.m. nitric oxide in 50 per cent relative humidity air (residence time 27·5 min)

The production of light-scattering aerosol from irradiated hydrocarbon–nitric oxide mixtures both in the absence and in the presence of sulfur dioxide

A cursory survey was made of the efficacy of various hydrocarbon types in producing aerosol under irradiation. Most of the hydrocarbons chosen are representative of the more common types expected to be found in polluted atmospheres. The following fixed conditions were chosen for this study: 3 p.p.m. hydrocarbon, 1 p.p.m. nitric oxide, 50 per cent relative humidity, and 27 min residence time. These conditions were deviated from in some experiments but were adhered to in at least one experiment for each hydrocarbon. Influent sulfur dioxide, when used, was generally in the range of 0·03–0·3 p.p.m.

The results obtained in the absence of sulfur dioxide are shown in Table 6. Among the hydrocarbons tested, only branched-chain internal olefins, *cyclo*-olefins, and diolefins were definitely capable of producing light-scattering material under these conditions. Of these, only the *cyclo*-olefin—in this case, *cyclo*hexene—showed light-scattering values comparable with those produced by some hydrocarbons in the presence of sulfur dioxide. A very small amount of scattering was shown by 1-pentene, but the amount was so small that the possible effect of impurities in the mixture cannot be disregarded.

The effect on the observed light scattering of adding sulfur dioxide to these same mixtures is shown in Table 7. The olefins tested, including *cyclo*-olefins and diolefins, were active in accelerating the disappearance of sulfur dioxide. The light scattering from irradiated mixtures of the olefins and diolefins was strongly enhanced by the addition of sulfur dioxide. Ethylene produced an uncertain marginal effect, probably related to its known low rate of photo-oxidation. The addition of sulfur dioxide to the irradiated *cyclo*hexene mixture had no large effect on the already large light scattering, although the upper limit of the range of variation was apparently increased from about 11 to about 23. Some of the saturated hydrocarbon and *p*-xylene nitric oxide mixtures apparently suppressed the appearance of aerosol completely. There are strong indications that some of these same mixtures may have enhanced rather than suppressed sulfur dioxide disappearance at the same time that no appreciable aerosol was being produced. This points to the presence in these systems of processes other

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TABLE 6. LIGHT SCATTERING AND TOTAL PARTICLE COUNT OBSERVED IN PHOTO-OXIDIZED MIXTURES OF 3 P.P.M. HYDROCARBON AND 1 P.P.M. NITRIC OXIDE WITH 50% R.H. AIR

Experiment number	Hydrocarbon	Residence time (min)	Light scattering referred to air	Particle count per ml	Light scattering at time of count
44 AS	Methane	27	0·00	NI	NI
34 AS	*n*-Pentane	27	0·00	NI	NI
32 AS	2-Methylbutane	27	0·00	NI	NI
35 AS	2, 2-Dimethyl propane	27	0·00	NI	NI
38 AS	*Cyclo*pentane	27	0·00	NI	NI
49 AS	Ethylene	27	0·00	NI	NI
25 AS	1-Pentene	27	0·04	NI	NI
23 AS	2-Methyl 1-propene	27	0·00	NI	NI
1 A-1	*Trans*-2-butene	21	0·00	NI	NI
18 AS	*Trans*-2-butene	27	0·00	NI	NI
21 AS	*Trans*-2-butene	27	0·00	NI	NI
2 A-2	2-Methylbutene-2	17	≳0·22	≳14	~0·22
3 A-2	2-Methylbutene-2	17	0·60	NI	NI
29 AS	2, 3-Dimethylbutene-2	27	0·19	NI	NI
30 AS	2, 3-Dimethylbutene-2	27	0·30	NI	NI
27 A	*Cyclo*hexene	27	0·26(ss)	179	7·6 (transient peak)
28 AS	*Cyclo*hexene	27	<11·1	290	11·1 (peak of light scattering)
31 AS	*Cyclo*hexene	27	10·8	NI	NI
41 AS	*Cyclo*hexene	27	8·2–14·2	NI	NI
22 AS	1, 3-Butadiene	27	0·38	NI	NI
47 AS	1-Butyne	27	0·00	NI	NI
42 AS	Benzene	27	0·00	NI	NI
50 AS	Toluene	27	0·00	NI	NI
48 AS	Ethyl benzene	27	0·00	NI	NI
40 AS	p-Xylene	27	0·00	NI	NI

NI means no information.

than co-photo-oxidation of sulfur dioxide to sulfuric acid. Methane, 2,3-dimethyl propane, 1-butyne, and benzene–nitric oxide mixtures had no great effect on the photo-oxidation of sulfur dioxide and the associated production of aerosol. Toluene and ethyl benzene may have strengthened the light scattering slightly, but there was no evidence of pronounced acceleration of sulfur dioxide disappearance.

Since all of these experiments were performed under arbitrarily fixed conditions with no or few replications, it is probable that there are conditions under which aerosol can be produced with and without sulfur dioxide in the presence of some of the inactive hydrocarbons. However, the results summarized above do bring out the marked activity of the olefins in this phenomenon.

TABLE 7. LIGHT SCATTERING AND TOTAL PARTICLE COUNT OBSERVED IN PHOTO-OXIDIZED MIXTURES OF 3 p.p.m. HYDROCARBON, 1 p.p.m. NITRIC OXIDE, AND SULFUR DIOXIDE WITH 50% R.H. AIR

Experiment number	Hydrocarbon	Residence time (min)	Sulfur dioxide concentration (p.p.m.)		Enhancement ratio[a]	Light scattering referred to air	Particle count	
			Influent	Effluent[a]			cm^{-3}	Light scattering[b]
44 AS	Methane	27	0·03–0·10	0·00	≲8·9	0·00		NI
44 AS	Methane	27	0·14	0·14	0·0	1·80		NI
34 AS	*n*-Pentane	27	0·03–0·10	0·00	≲8·9	0·00		NI
34 AS	*n*-Pentane	27	0·14	0·15	0·0	0·00		NI
32 AS	2-Methylbutane	27	0·03–0·10	0·01	≲8·0	0·00		NI
33 AS	2-Methylbutane	27	0·03–0·10	0·01	≲8·0	0·00		NI
35 AS	2, 2-Dimethyl propane	27	0·03–0·10	0·00	≲8·9	0·00		NI
35 AS	2, 2-Dimethyl propane	27	0·14	0·01	≲8·3	0·22		NI
38 AS	*Cyclo*pentane	27	0·03–0·10	0·00	≲8·9	0·00		NI
38 AS	*Cyclo*pentane	27	0·14	>0·08	<3·8	0·00		NI
49 AS	Ethylene (6 p.p.m.)	27	0·03–0·10	0·00	≲8·9	0·06		NI
49 AS	Ethylene (6 p.p.m.)	27	0·14	0·16	0·0	2·70		NI
25 AS	1-Pentene	27	0·27	0·14	4·3	7·7–13·6	172	7·8
23 AS	2-Methyl 1-propene	27	0·27	0·19	2·6	2·0– 6·9	17	1·6
1 A-2	*Trans* 2-butene	21	0·47	NI	NI	16	248	~16
18 AS	*Trans* 2-butene	27	0·61	0·36	3·6	16·1		NI
21 AS	*Trans* 2-butene	27	0·27	0·00	8·9	≳10·5		NI
21 AS	*Trans* 2-butene	27	0·39	0·29	2·3	16·1	710	16·1
2 A-3	2-Methylbutene-2	17	0·47	NI	NI	6·4	511	6·4
3 A-3	2-Methylbutene-2	17	0·09	NI	NI	6·2	240	6·2
3 A-4	2-Methylbutene-2	17	0·19	NI	NI	11·8	590	11·8
3 A-5	2-Methylbutene-2	17	0·47	NI	NI	18·3	900	18·3
29 AS	2, 3-Dimethylbutene-2	27	0·27	0·00–0·11	<5·3	2·0– 6·3	22	2·0
30 AS	2, 3-Dimethylbutene-2	27	0·09	0·00	8·9	17·9		NI
28 AS	*Cyclo*hexene	27	0·27	≲0·06	≳6·9	3·8–23·4	129	6·4
31 AS	*Cyclo*hexene	27	0·03–0·10	0·00	8·9	6·4–13·1		NI
22 AS	1, 3-Butadiene	27	0·27	0·15	6·9	16·7	509	13·8
47 AS	1-Butyne	27	0·03–0·10	0·00	8·9	0·00		NI
47 AS	1-Butyne	27	0·14	0·14	0·0	0·11		NI
42 AS	Benzene	27	0·03–0·10	0·00	8·9	0·06		NI
42 AS	Benzene	27	0·14	>0·13	0·0	0·98		NI
50 AS	Toluene	27	0·03–0·10	0·00	8·9	0·00		NI
50 AS	Toluene	27	0·14	0·05–0·35	?	2·00		NI
48 AS	Ethyl benzene	27	0·03–0·10	0·00	8·9	0·00		NI
48 AS	Ethyl benzene	27	0·14	0·16	0·0	2·70		NI
40 AS	*p*-Xylene	27	0·03–0·10	0·00	8·9	0·00		NI
40 AS	*p*-Xylene	27	0·14	0·08	3·8	0·00		NI

NI means no information.

[a] Measurements of effluent sulfur dioxide concentration and values of the enhancement ratio calculated from these measurements are in considerable doubt, particularly at the lower influent sulfur dioxide concentrations because of difficulties in establishing and measuring low concentrations in the apparatus. The enhancement ratio is the ratio of rate of disappearance of sulfur dioxide to that expected from sulfur dioxide photo-oxidation alone and can be no greater than 8·9 at a residence time of 27 min if the photo-oxidation rate is 0·0046 min^{-1}.

[b] This column gives light scattering at the time the count was made.

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The authors prefer to neglect (7) pending proof that ozone can be formed. This mechanism, plus the observed independence of oxygen concentration, requires a quantum yield of 2 in contrast with the fractional yields actually observed. This inconsistency can be avoided by taking advantage of some recent developments in the theory of electronically excited AB_2 molecules.

Molecular orbital calculations by WALSH (1953) indicate that the first excited electronic state of sulfur dioxide is a " bent " state, having a different O–S–O bond angle than the ground electronic state. By the Franck–Condon principle, then, the absorption of radiation by sulfur dioxide promotes it into a highly excited vibrational state of the second electronic level, thus complicating somewhat the process represented by (1), (2) and (3). This vibrational ground state can probably be identified with the reactive species of reactions (4) and (6) and we can write

$$SO_2 + h\nu \rightarrow SO_2^{**} \tag{9}$$

$$SO_2^{**} \rightarrow SO_2 \quad \text{by various processes} \tag{10}$$

$$SO_2^{**} \rightarrow SO_2^{*} \quad \text{by various processes} \tag{11}$$

$$SO_2^{*} \rightarrow SO_2 \quad \text{by various processes.} \tag{12}$$

The bent state can probably be considered to be a biradical having an unpaired electron in a sulfur sp^3 orbital, thus facilitating reaction (6). The only condition on relative rates imposed by experimental findings is that reaction (6) be much more rapid than the net rate of processes (12) at oxygen pressures greater than about 50 mm. Therefore, the bent ground state is sufficiently stable with regard to collisional deactivation and spontaneous or induced radiation so that it reacts nearly completely with oxygen at these relatively high oxygen partial-pressures and at total pressures ranging from 0·1 to 1 atmosphere. Considerably more work is indicated on the photodismutation and photo-oxidation of sulfur dioxide before the mechanism can be stated in detail with confidence.

The work described in this paper suggests that the reaction

$$SO_4 + NO \rightarrow SO_3 + NO_2 \tag{13}$$

takes place, thus accounting for the possible suppressing effect on the sulfur dioxide photo-oxidation rate by nitric oxide.

In the presence of photolyzing nitrogen dioxide, both reaction (13) and the reaction

$$M + SO_2 + O \rightarrow SO_3 + M \tag{14}$$

must be considered.

Sulfur dioxide at parts per million concentrations cannot compete so successfully with molecular oxygen in air for oxygen atoms as to account for the observed enhancement of dioxide consumption by co-photo-oxidizing olefin–nitric oxide mixtures. Therefore, reaction (14), plus

$$NO_2 + h\nu \rightarrow NO + O \tag{15}$$

and

$$O + O_2 + M \rightarrow O_3 + M \tag{16}$$

plays only a minor role ($R_{14} \simeq 3 \times 10^3$ (SO_2) (O) p.p.m. min^{-1}, $R_{15} = 1{\cdot}2$ (NO_2) p.p.m. min^{-1},* $R_{16} \simeq 1{\cdot}4 \times 10^6$ (O) p.p.m. min^{-1} with air at atmospheric pressure in the 50-l.

* This nitrogen dioxide photolysis rate was calculated from the data in Fig. 1 and BLACET and HALL's values of the absorption coefficients and quantum efficiency for nitrogen dioxide (LEIGHTON, 1956, pp. 50–54.

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reactor). (Nitric oxide is partially converted to nitrogen dioxide during the photo-oxidation.) We must, therefore, look elsewhere for the responsible reactive species. For example, we may write speculatively

$$RO_2 \cdot + SO_2 \rightarrow RO \cdot + SO_3, \tag{17}$$

but more experimental work is needed before a mechanism can be confidently proposed.

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DIE WESTDEUTSCHEN MASSNAHMEN ZUR REINHALTUNG DER LUFT:

DIE "KOMMISSION REINHALTUNG DER LUFT", IHR ARBEITSPROGRAMM UND IHRE BISHERIGE TÄTIGKEIT

KARL SCHWARZ
Technischer Überwachungs-Verein, Essen
(*Received* 3 *December* 1959)

Zusammenfassung—Der Beitrag befaßt sich mit den Bemühungen zur Verringerung der Luftverschmutzung in Westdeutschland, speziell mit der Arbeit der "Kommission Reinhaltung der Luft" und den bisherigen Ergebnissen ihrer Arbeit.

Der auf Anregung der "Interparlamentarischen Arbeitsgemeinschaft" gegründeten "Kommission Reinhaltung der Luft" gehören Vertreter aller an der Luftverschmutzung interessierter Kreise an, und zwar sowohl der Verschmutzer als auch der Betroffenen. Wissenschaft und Technik sind gleicherweise vertreten. Die Kommission arbeitet für jedes Verschmutzungsproblem "*Technische Richtlinien*" aus, in welchen Maßnahmen zur Verringerung der Verschmutzung zusammengestellt und zulässige Grenzwerte festgelegt werden. Ein Rahmengesetz soll diesen "Technischen Richtlinien" die nötige Verbindlichkeit geben. Diese Regelung hat den Vorteil, daß die "Richtlinien" mit dem Gewinn neuer Erfahrungen in einfacher Weise dem jeweils neuesten Stand der Wissenschaft und Technik angepaßt werden können, ohne daß die Maschinerie der Gesetzgebung bemüht werden muß.

Im Sinne des *Nachbarschutzes* soll die Beurteilung der Zulässigkeit eines *Auswurfes an schädigenden oder belästigenden Stoffen* (*Emission*) soweit irgend möglich an Hand der *Wirkungen* dieses Stoffes erfolgen, d.h., daß als Ausgangspunkt für die Auswurfbegrenzung der *zulässige Niederschlag bzw. die zulässige Konzentration dieser Stoffe in der Nachbarschaft des Werkes* (*Immission*) entscheidend ist.

Die Kommission mußte daher auf folgenden Hauptgebieten tätig werden:

1. Studium der *Meßverfahren* für die einzelnen Emissions-bzw. Immissionskomponenten. Ausarbeitung von *Richtlinien zur Festlegung einheitlicher, genügend gesicherter Meßmethoden.*
2. Studium der *Wirkungen* der verschiedenen emittierten Stoffe auf Lebewesen und Baustoffe, Ausarbeitung von *Richtlinien für zulässige Grenzwerte der Luftverunreinigung in der Atemluft* (MIK-Werte = *max. Immissions-Konzentrationswerte*).
3. Studium der *Ausbreitung von Gasen und Stäuben in der Atmosphäre*, insbesondere des Zusammenhangs zwischen dem Auswurf (Emission) und der Konzentration am Nachbargrundstück (Immission). Erarbeitung von *Richtlinien zur Ausbreitungsrechnung*.
4. Studium der Möglichkeiten zur *Verringerung des Auswurfes* an schädlichen oder belästigenden Stoffen, Festlegung von Zulässigkeitsgrenzwerten unter Beachtung der unter 2. und 3. genannten Zusammenhänge (*Auswurf-Richtlinien*).

Da auf vielen Teilgebieten dieses weitgespannten Arbeitsgebietes die Erfahrungen des In- und Auslandes zur Aufstellung rechtlich verbindlicher Richtlinien nicht ausreichten, wurde ein—fortlaufend ergänztes—*Forschungsprogramm* aufgestellt, um die vorhandenen Lücken unserer Kenntnisse auf den vier oben beschriebenen Sektoren zu schließen. Die Arbeiten, über deren Stand und Umfang berichtet wird, sind in großem Umfang angelaufen und haben die ersten Ergebnisse gebracht.

Als Ergebnis aller dieser Bemühungen kannte bereits *eine Reihe von Richtlinien der Öffentlichkeit übergeben werden*, die für einige der wichtigsten Luftverschmutzer (Dampfkesselanlagen, Erzsint-

eranlagen, Zementwerke und andere) Maßnahmen zur Auswurfverringerung enthalten und die zulässigen Auswürfe begrenzen. Eine Reihe weiterer Richtlinien für Auswürfe industrieller Anlagen, Hausbrand und Kleinfeuerungen stehen vor der Fertigstellung, ebenso auch Richtlinien für zulässige Konzentrationen schädlicher Stoffe in der Atemluft (Schwefeldioxyd, Schwefelwasserstoff und nitrose Gase). Auch die ersten meßtechnischen Richtlinien und vorläufige Richtlinien für die Anwendung der Ausbreitungsrechnung gehen ihrer Vollendung entgegen.

Das entsprechende Rahmengesetz ist inzwischen vom Bundestag verabschiedet worden (1), so daß der Anwendung der " Richtlinien " nichts mehr im Wege steht.

Abstract—The paper reviews the efforts made in Western Germany to reduce air pollution and describes the work done by the " Commission for Clean Air " and its achievements to date.

On the initiative of the " Interparliamentary Working Party ", the Commission for Clean Air was formed in 1957. On it are represented the main producers of air pollution and also those who suffer from it, as well as scientists and technologists. The Commission elaborates technical " Regulations " in which measures for reducing pollution are given and maximum permissible concentrations are defined.

A general covering act ensures that these regulations have the force of law.

This has the advantage that the regulations can, from time to time, be altered so as to represent continuously the latest stage of knowledge in science and technology without having to involve, every time, the machinery of passing a new law.

As far as possible, the permitted concentrations of materials which are harmful or constitute a nuisance (emission) are based on their effects elsewhere and are hence based on permissible concentrations in the neighbourhood of the source. The actual concentrations of pollution in the air is called the immission.

The Commission has worked in the following four fields:

1. Study of methods of measurement for the different components of emission or immission: Regulations defining uniform and sufficiently reliable methods of measurement.
2. Study of the effects of the different materials emitted on organisms and building materials. Regulations covering maximum permitted concentrations in air (Mik values = maximum immission Konzentration).
3. Study of the dispersal of gases and dust in the atmosphere, in particular the relationship between emission and concentration in the neighbourhood (immission): Regulations for calculating dispersion of pollutants.
4. Study of possibilities for reducing emission of noxious or nuisance materials: Regulations covering emission concentrations with reference to the results obtained under (2) and (3) above.

In many detailed parts of this wide field of work there does not exist sufficient information in Germany or abroad to justify laying down regulations which have the force of law. Therefore a *programme of research* was set up, and is continually kept under review, in order to fill the gaps of knowledge in the four sections described above.

The paper describes in which fields work is going on and gives the first results obtained.

As a result of all these efforts, a number of regulations have been published which describe methods of reducing emission and state maximum allowable concentrations of emission for some of the most important sources of pollution, i.e. steam boilers, ore sinter plants, cement factories and others. Further regulations are nearly finished. These cover emission from industrial and domestic heating installations and permissible concentrations of noxious gases in air (sulphur dioxide, hydrogen sulphide and nitrous oxides). The first regulations for methods of measurement and interim regulations for calculating dispersion are also nearing completion.

The corresponding covering general Act has, in the meantime, been passed by the Federal Government so that the way for enforcing the regulations is now clear.

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1. ENTSTEHUNG UND ZUSAMMENSETZUNG DER "KOMMISSION REINHALTUNG DER LUFT"

NACHDEM die Diskussion über die Luftverunreinigung in der Öffentlichkeit immer breiteren Raum eingenommen hat, gründete der " Verein Deutscher Ingenieure "

(VDI) auf Anregung der " Interparlamentarischen Arbeitsgemeinschaft "* im November 1955 den " Ausschuß Reinhaltung der Luft in der VDI-Fachgruppe Staubtechnik ". Der Ausschuß übernahm es, die mit der Luftverunreinigung verbundenen Fragen auf allen von ihr betroffenen Gebieten zu untersuchen und Vorschläge zur

Bild 1. Organisatorischer Aufbau der Kommission Reinhaltung der Luft.

* Der " Interparlamentarischen Arbeitsgemeinschaft " (IPA) gehören rund 300 Abgeordnete und Kabinettsmitglieder des Bundes und der Länder aus allen Parteien an. Ihre Aufgaben sind: die Förderung der interparlamentarischen und interfraktionellen Zusammenarbeit, die Zusammenstellung der notwendigen Unterlagen und die laufende Unterrichtung der Mitglieder über alle einschlägigen Fragen. Die Mitglieder der Interparlamentarischen Arbeitsgemeinschaft beschließen dementsprechend gemeinsam zu ergreifende Initiativmaßnahmen in den Parlamenten.

Verbesserung der Verhältnisse und zur Sicherung einer wirksamen Luftkontrolle auszuarbeiten. Da sich sehr bald herausstellte, daß seine Arbeiten weit über das Gebiet der Staubtechnik hinausgehen, wurde der Ausschuß 1957 in die selbständige "*Kommission Reinhaltung der Luft*" unter Hinzuziehung möglichst aller an dem Problem interessierter Kreise umgewandelt, deren Federführung der VDI übernahm.

In der Kommission wirken u.a. Sachverständige folgender Vereinigungen und Stellen mit:

Deutsche Gesellschaft für Hygiene und Mikrobiologie—Gesellschaft Deutscher Chemiker.

Deutscher Wetterdienst—Gesellschaft Deutscher Metallhütten und Bergleute—Steinkohlenbergbauverein-Technische Überwachungs-Vereine—Verein Deutscher Eisenhüttenleute—VDI-Fachgruppe Staubtechnik—Vereinigung der Großkesselbesitzer.

Wissenschaftler von Hochschulen und Instituten für Biologie, Chemie, Forst- und Landwirtschaft, Medizin, Meteorologie, Physik, Technik.

Bundesverband der deutschen Industrie (verschiedene Industriegruppen)—Deutsche Bundesbahn—Straßenverkehr.

Deutscher Bauernverband—Kommunale Spitzenverbände—Siedlungsverband des Ruhrkohlenbezirks.

Zuständige Ministerien—behördliche Überwachungsorgane.

Den organisatorischen Aufbau der Kommission zeigt Bild 1.

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2. ARBEITSGRUNDSÄTZE

Bei der Aufnahme der Arbeiten mußte sich die Kommission mit einigen grundsätzlichen Fragen auseinandersetzen. Dazu gehörten die Entscheidungen

(a) über die *Art der zu schaffenden Vorschriften*,
(b) über den *Umfang* derselben und endlich
(c) über den *Ausgangspunkt* für die Beurteilung von Luftverschmutzern.

Zu (a): In der ersten Frage kamen uns die Erfahrungen zugute, die man im Ausland mit gesetzlichen Maßnahmen zur Verbesserung der Luftverhältnisse gemacht hat. Es hat sich gezeigt, daß ein so heterogener Fragenkomplex sich nicht dazu eignet, in den starren Zwang eines umfassenden Luftreinheitsgesetzes mit festgelegten Beurteilungsvorschriften und Begrenzungswerten eingepaßt zu werden. Eine derartige Regelung muß sich notwendigerweise mit der weiteren Entwicklung entweder hemmend auf den technischen Fortschritt auswirken, oder sie führt zu einer—geduldeten—Mißachtung des Gesetzes. Wir haben daher den Weg über die Schaffung "*technischer Richtlinien*" eingeschlagen, die für jedes einzelne Verschmutzungs problem dem jeweiligen Stand der Wissenschaft und Technik entsprechend aufgestellt werden und die im Rahmen eines zur Zeit vom Deutschen Bundestag bearbeiteten *Gesetzes zur Verbesserung des Nachbarschutzes* (1) die nötige Verbindlichkeit erhalten sollen.† Mit dem Gewinn neuer Erfahr-

† Das Gesetz ist inzwischen vom Deutschen Bundestag verabschiedet worden. Der Wortlaut ist in (1) enthalten.

ungen können diese Richtlinien mühelos verbessert und dem neuesten Stand der Technik angepaßt werden, ohne daß hierzu die schwerfällige Maschinerie der Gesetzgebung in Gang gesetzt werden muß.

Zu (b): Der Umfang der Arbeiten war durch den Kreis der Luftverschmutzer gegeben. Es war selbstverständlich, daß aus Billigkeitsgründen alle Luftverunreiniger in den Kreis der Überlegungen einbezogen werden müssen, wie es der von der Kommission herausgegebene " *Katalog der Luftverunreiniger* " erkennen läßt (2). Das Werk soll als Gemeinschaftsarbeit aller, sowohl der Verunreiniger als auch der von der Verunreinigung Betroffenen, entstehen. Für den Beginn der Arbeiten war natürlich eine Auswahl zu treffen, welche wichtigsten Emissionsprobleme einer vordringlichen Bearbeitung bedürfen.

Zu (c): Der rechtliche Schutz des Nachbarn bezieht sich auf die *Wirkungen* der emittierten Stoffe auf das Nachbargrundstück, also auf die Wirkungen, die von den *Immissionen (das ist den in Bodennähe in bestimmter Konzentration in der Atemluft enthaltenen oder auf dem Erdboden niedergeschlagenen Emissionsstoffen*, seien es Gase, Flüssigkeitströpfchen oder Stäube) ausgehen. Die Kommission hat sich entschlossen, wo irgend möglich, den rechtlich exakten Weg einzuschlagen und die *Immission zum Ausgangspunkt für die Beurteilung von Verschmutzungsfragen* zu machen. Mit diesem Entschluß wurden bewußt große Schwierigkeiten in Kauf genommen. Diese Art der Beurteilung verlangt nämlich:

(a) die Festlegung von Zulässigkeitswerten für die Immission (zulässige Staub- und Gasgrenzkonzentrationen oder -niederschlagswerte),

(b) die Festlegung der Auswurfbedingungen nach diesen Zulässigkeitswerten, d.h. den Rückschluß von der Immission auf die Emission, von dem Betroffenen auf den Verursacher.

3. DAS ARBEITSPROGRAMM

Aus dem oben Erwähnten ergeben sich vier Schwerpunkte für die Arbeit der Kommission:

1. Wenn Begrenzungsvorschriften (für die Immission oder die Emission) aufgestellt werden, müssen die genannten Werte zunächst mit genügender Genauigkeit *meßbar* sein. Als erstes waren daher die vorhandenen Meßmethoden auf ihre Brauchbarkeit, d.h. vor allem auf ihre Genauigkeit und Betriebssicherheit zu prüfen und neue Meßmethoden zu entwickeln, wo die vorhandenen nicht ausreichten.
2. Es war zu klären, welche *Wirkungen* von bestimmten Konzentrationen bzw. Niederschlägen der zu betrachtenden Immissionsstoffe auf Mensch, Tier und Pflanze ausgehen. Das Ziel dieser Untersuchungen ist die Erarbeitung von Grenzwerten für die einzelnen belästigenden oder schädigenden Immissionskomponenten (MIK-Werte*), die nicht überschritten werden sollten.
3. Die Immissionswerte müssen in Zusammenhang gebracht werden mit der Auswurfstelle, der Emission. Eine weitere Gruppe von Arbeiten beschäftigt sich

* MIK = " maximale Immissions-Konzentration ", analog zu der gebräuchlichen Bezeichnung der " maximalen Arbeitsplatz-Konzentration " = MAK.

daher mit dem Problem der *Ausbreitung von gas- und staubförmigen Emissionen in der Atmosphäre*. Ihr Ziel ist die Ermöglichung eines Rückschlusses von der zulässigen Immission auf die zulässige Emission bzw. die Festlegung der Auswurfbedingungen (Auswurfmenge und Konzentration, Schornsteinhöhe, Austrittsgeschwindigkeit), die eingehalten werden müssen, wenn eine bestimmte Grenzimmission nicht überschritten werden soll.

4. Endlich sind die *Auswurfbedingungen* für die einzelnen Emittentengruppen auszuarbeiten, welche eingehalten werden müssen, um mit den vorhandenen technischen Mitteln die mit Rücksicht auf die Wirkung der Emission zu stellenden Forderungen zu erfüllen. Hierzu gehört auch das Studium der Möglichkeiten, bei den verschiedenen Fabrikationsverfahren die Anteile schädlicher oder belästigender Gase und Stäube in den Abgasen herabzusetzen bzw. neue Zusatzverfahren zur Abscheidung dieser Stoffe auszuarbeiten.

Das Arbeitsprogramm der Kommission wird also im wesentlichen von den vier Arbeitsgruppen:

I. *Meßtechnik*,
II. *Zulässigkeitswerte für die Immission*,
III. *Zusammenhang zwischen Emission und Immission*,
IV. *Auswurfgrenzwerte*,

durchgeführt.

Diese Übersicht zeigt, wie verschiedenartig die Aufgaben sind und welch weites Gebiet der Wissenschaften sie umspannen.

Verbindliche Vorschläge für die Begrenzung des Auswurfes von Industrieanlagen können erhebliche wirtschaftliche Folgen für die betroffenen Industrien haben. Es ist daher nur billig, daß stichhaltige und gesicherte Unterlagen für die Beurteilung jedes einzelnen Emissionsproblems gefordert werden. Bei Inangriffnahme der Arbeiten war es daher zunächst notwendig, für die behandelten Auswurfprobleme den derzeitigen *Stand der Wissenschaft und Technik* festzustellen und darauf alle weitere Arbeit aufzubauen. Zur Erfüllung dieser Forderung wurde der folgende Weg beschritten:

(a) Zur Mitarbeit werden sowohl die einschlägige *Wissenschaft* (Hochschulinstitute, Forschungsanstalten, Wissenschaftler) als auch die *Praxis* (Hersteller und Betreiber, Überwachungs- und Beratungsorganisationen) herangezogen.
(b) Allen Arbeiten geht ein sorgfältiges Studium der *Literatur* sowohl des In- als auch des Auslandes voraus. Wo es notwendig oder erwünscht ist, wird der Kontakt mit in- und ausländischen Forschungsstellen und Forschern aufgenommen.

Das Studium der einzelnen Probleme zeigt, wo noch Lücken in unserer Erkenntnis offen sind. Hier müssen *Forschungsarbeiten* einsetzen. Es ist Aufgabe der Kommission, die zu lösenden Probleme klar herauszuarbeiten, geeignete Forschungsstellen oder Forscherpersönlichkeiten für die einzelnen Probleme zu finden und alle diese Arbeiten mit unseren Arbeiten und den Arbeiten anderer, auch ausländischer Stellen zu koordinieren und—nicht zuletzt—für die Finanzierung zu sorgen.

So entstand die *Forschungsgruppe*, die die Forschungsarbeiten betreut und koordiniert.

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4. DIE FORSCHUNGSAUFGABEN DER KOMMISSION REINHALTUNG DER LUFT

Die Forschungsaufgaben, die von der Kommission angeregt, unterstützt oder ausgeführt werden, erstrecken sich über den gesamten Tätigkeitsbereich und lassen sich am besten verfolgen, wenn wieder die vier Arbeitsschwerpunkte betrachtet werden.

Meßmethoden

(*a*) *Gas.* Bei der Erfassung des Anteiles an *schädlichen oder belästigenden Gasen in der Atemluft* liegt die Schwierigkeit—auf der Immissionsseite—darin, daß Konzentrationen in der Größenordnung von Bruchteilen von mg je m³ mit genügender Sicherheit gemessen werden müssen, da einige Gase bei so niedrigem Anteil bereits schädigende Wirkungen auslösen. Dazu kommt, daß die Konzentrationen im Hauptimmissionsgebiet unterhalb der Rauchfahnen oft sehr stark schwanken. Da es notwendig ist, die Reaktion des Betroffenen, z.B. der Pflanze, auf kurze Konzentrationsstöße zu berücksichtigen, muß der *zeitliche Verlauf der Konzentration* mit möglichst geringer Integrationszeit erfaßt werden.

Im Vordergrund steht das Problem der Messung von SO_2, der wichtigsten gasförmigen Immissionskomponente. Es wurde als erstes in Angriff genommen. Als Ergebnis stehen heute bereits anzeigende und registrierende Geräte für SO_2-Konzentrationen in der Größenordnung von 0,1 bis 2,5 mg/m³ mit genügender Meßgenauigkeit zur Verfügung. Ähnliche Arbeiten laufen für die selektive Messung von SO_3, für H_2S, für Stickoxyde und Fluor.

Demgegenüber macht die Messung von *Gaskonzentrationen auf der Auswurfseite*—bei den relativ hohen Konzentrationen—keine allzu große Schwierigkeit, wenn auch die geforderten registrierenden Betriebsgeräte zur *Dauerüberwachung der Emissionen*, z.B. des SO_2-Auswurfes, noch einer speziellen Erprobung im Dauerbetrieb bedürfen. Eine besondere Stellung nehmen die *Abgase von Kraftfahrzeugen* ein. Bei ihnen kommt es u.a. darauf an, mit einfachen Meßgeräten schädliche Abgasbestandteile, wie z.B. den CO-Gehalt, den Gehalt an unvollständig verbrannten Kraftstoffresten, den Rüssgehalt zu messen. Damit soll die Möglichkeit einer laufenden Kontrolle der richtigen Einstellung von Motoren, z.B. bei dem routinemäßigen Wartungsdienst, geschaffen werden, um den Anteil dieser schädlichen oder belästigenden Gase auf ein Minimum herabzusetzen.

(*b*) *Staub.* Zur *registrierenden Messung des Staubgehaltes in stromenden Gasen* auf der Emissionsseite sind an mehreren Stellen Geräte entwickelt worden. Sir werden jetzt im Industrieeinsatz erprobt. Das Ziel ist, größere Emittenten mit derartigen Geräten auszurüsten, um eine dauernde Kontrolle des Auswurfes zu ermöglichen und damit die beste Wirkungsweise der Entstaubungseinrichtungen zu sichern.

Immissionsseitig sind in der Konzentrationsmessung entscheidende Erfolge erzielt worden. Dabei interessieren uns nicht so sehr die Geräte zur Bestimmung der Teilchenzahl in der Raumeinheit. Wir benötigen für die weitere Verwertung *Gewichtsangaben über die Staubkonzentration in der Atemluft.* Auch hier liegt die Schwierigkeit wieder in der Bestimmung der oft sehr geringen Staubkonzentration in der Außenluft (z.B. um 0,1 bis 1 mg/m³). Es mußten geeignete Filter entwickelt werden, wobei ein Einfluß einer eventuellen Gasadsorption am Filter noch zu klären ist.

Schwierig sind die Verhältnisse bei der *Staubniederschlagsmessung.* Zur Verfügung stehen einmal die Staubhaftfolien. Sie eignen sich besonders für Großzahl-

messungen und kurze Meßzeiten und stellen damit ein wertvolles Hilfsmittel zur Kontrolle und Anwendung der Ausbreitungsrechnung dar, da diese nur über Zeiten mit genügend konstanten meteorologischen Verhältnissen durchgeführt werden kann und ein dichtes Meßstellennetz erfordert. Demgegenüber eignen sich die Niederschlagstrichter verschiedener Bauformen schon aus Kostengründen besser für Meßvorhaben mit wenigen Meßstellen und längeren Meßzeiten.

Die mit den verschiedenen Meßgeräten gewonnenen Ergebnisse lassen sich noch nicht eindeutig vergleichen. In einer großangelegten systematischen Arbeit, in welcher die physikalischen Voraussetzungen der Messung untersucht und die Geräte in einem Langzeitvergleich bei verschiedenen meteorologischen Bedingungen nebeneinander eingesetzt werden, sollen die Unterschiede geklärt und der Weg zu Standard-Meßgeräten mit bekannten Fehlergrenzen unter Absteckung des zugehörigen Einsatzbereiches vorbereitet werden.

Immissions-Grenzwerte (*Schädlichkeitsgrenzen*)

Hier handelt es sich nicht nur um eines der schwierigsten Arbeitsgebiete, sondern auch um eine Aufgabe, die das größte Verantwortungsbewußsein der Beteiligten voraussetzt. Wenn es bei der Frage der zumutbaren *Belästigung* durch bestimmte Immissionen (Stäube, Gerüche) noch einen gewissen Spielraum in den Betrachtungen geben darf, so kann man diesen nicht mehr zulassen, wenn es sich um *Schädigungen* der Gesundheit des Menschen handelt. Das gilt in fast ebenso verantwortlicher Weise für die Schädigung von Tieren und der Vegetation.

Auf diesem Gebeit, besonders auf dem der Pflanzenschädigung durch Einwirkung von Gasen, ist bereits viel gearbeitet worden. Ein sorgfältiges Studium der Literatur, insbesondere auch der des Auslandes, führte aber zu der Erkenntnis, daß nur die wenigsten Ergebnisse genügend allgemeine Aussagekraft haben, wie sie für die Festlegung rechtlich verbindlicher Zulässigkeitswerte gefordert werden muß.

Im Vordergrund steht die *Wirkung des SO_2 auf Pflanzen*, deren Ansprechempfindlichkeit wesentlich größer ist als bei Mensch und Tier. Nach umfangreichen Vorarbeiten lief eine großangelegte Versuchsserie an, die die Fragen der unterschiedlichen Empfindlichkeit der verschiedenen interessierenden Pflanzensorten gegenüber der SO_2-Begasung und den Einfluß der Begasungszeit, insbesondere auch der kurzzeitigen Spitzenbegasung, in Zusammenhang mit den Lebensbedingungen, den Umweltfaktoren, besonders auch den im Wachstum der Pflanze unterschiedlichen Funktionszeiten (Tag und Nacht, Sommer und Winter, Blattknospen—Fruchtzeit) klären soll. Drei Versuchsreihen sollen dazu dienen:

(a) Die *Naturversuche* in Biersdorf, in der Nähe eines industriellen Emittenten von SO_2, in welchen die Pflanzen unter natürlichen Lebens- und Umweltbedingungen in der in Industrienähe tatsächlich auftretenden Art (schwankende Konzentrationen), also in *natürlicher* Weise begast werden.

(b) Die Freilandversuche in Hattersheim, in welchen bei *natürlichen* Lebens- und Umweltbedingungen *künstliche* Begasungen definierter und gleichbleibender Stärke und bestimmter Dauer, insbesondere auch Spitzenbegasungen angewendet werden.

(c) Versuche in Klimakammern, bei welchen unter definierten *künstlichen* Lebensbedingungen definierte und gleichbleibende—*künstliche*—Begasungen angewendet werden.

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In der Klimakammer sollen die Zusammenhänge zwischen der definierten Gaskonzentration und Begasungszeit einerseits und ihrer Wirkung auf die Pflanze andererseits festgestellt werden. Die Versuche in Hattersheim dienen zur Übertragung der Ergebnisse der Laborversuche auf das Freiland, immer noch bei definierter, gleichbleibender Begasungsstärke. Die Biersdorfer Versuche endlich sollen es ermöglichen, die Ergebnisse der Klimakammer und der Freilandversuche (bei konstanter Begasung) auf die in der Natur wirklich vorhandenen Verhältnisse zu übertragen.

Nach dem jetzigen Stand der Arbeiten ist die Hoffnung berechtigt, in absehbarer Zeit Ergebnisse vorlegen zu können, wobei sich wahrscheinlich der Zusammenhang zwischen den zulässigen Konzentrationen und der Einwirkungszeit in Kurvenform darstellen wird.

Neben den Untersuchungen im Pflanzensektor stehen Untersuchungen der *Wirkung von SO_2 auf Tiere* (u.a. an Tierzellen) *und auf den Menschen*. Diese Untersuchungen sollen—ebenso wie die Pflanzenversuche—später auch auf *andere Gasarten* ausgedehnt werden. Im Vordergrund stehen dabei die Stickoxyde, dann Schwefelwasserstoff, Merkaptane, Chlor und endlich Fluor.

Statistische Erhebungen über den *Einfluß der Großstadtluft* auf den Gesundheitszustand besonders empfindlicher Menschengruppen (Kleinkinder, ältere Menschen) führen bereits in das Gebeit *kombinierter Einwirkungen*, d.h. Einwirkungen mehrerer Einzelkomponenten (Stäube und Gase, Aerosole). Dabei kann bekanntlich u.U. eine vielfache Steigerung der Reizwirkung des einzelnen Gases eintreten, verursacht durch die besondere Art der Verteilung in der Atmosphäre (Adsorption des Reizstoffes an Schwebstoffen, dadurch örtlich hohe Reizstoffkonzentrationen) oder durch Wechselwirkung mit anderen Verschmutzungskomponenten (Stickoxyde mit unvollständig verbrannten Kraftstoffresten). In Anlehnung vor allem an amerikanische Arbeiten muß daher den Fragen der *Smog*bildung und der Wirkung des Smogs besondere Aufmerksamkeit geschenkt werden.

Neben den Wirkungen der Gase beschäftigen wir uns natürlich auch mit denen der *wichtigsten Industriestäube* auf Mensch, Tier und Pflanze. Auch auf diesem Gebiet läuft eine Reihe von Arbeiten, die sich mit den Wirkungen der mengenmäßig im Vordergrund stehenden Flugstäube aus der Verbrennung von Stein- und Braunkohle und aus Zementwerken beschäftigen.

Ausbreitung von Gasen und Stäuben in der Atmosphäre

Für die Ausbreitung emittierter Gase und Stäube in der Atmosphäre bis zur betrachteten Immissionsstelle sind die vielfältigen und oft schwer zu erfassenden Einflüsse der Atmosphäre und der Bodengestaltung ausschlaggebend (z.B. Wind, Temperaturverhältnisse, Austauschverhältnisse, Bodenrauhigkeit). Gute Ansätze für die " Ausbreitungsrechnung " sind bereits vorhanden (3) und (4). Die von uns eingeleiteten bzw. angeregten Arbeiten dienen den Ziel, Unterlagen für eine genügend sichere Anwendung der Ausbreitungsrechnung unter den bei uns herrschenden meteorologischen Verhältnissen zu beschaffen. Es liegt in der Natur der Sache, daß diese Arbeiten vor allem langzeitige Messungen bei den verschiedensten meteorologischen Verhältnissen und an den verschiedensten Orten bedingen. Das Studium der ungünstigen Wetterlagen, bei welchen besonders hohe Immissionswerte auftreten können, wie z.B. der Inversion (in Zusammenhang mit dem Auftreten des gefährlichen Smog) liegt uns dabei besonders am Herzen. In diesem Zusammenhang wird auch die Frage

der richtigen Einbeziehung der *Schornsteinüberhöhung* in die Ausbreitungsrechnung durch eine umfangreiche experimentelle und theoretische Untersuchung geklärt.

Auswurfbegrenzung

Die Bedingungen, die an den Auswurf gestellt werden, führen in den meisten Fällen zu einer Kombination der zulässigen Auswurfmenge mit der notwendigen Schornsteinhöhe und gegebenenfalls der Auswurfgeschwindigkeit. Natürlich ist es unser besonderes Anliegen, den Auswurf an schädlichen oder belästigenden Stoffen überhaupt so weit wie möglich herabzusetzen. Dieser Aufgabe ist die letzte Gruppe unserer Forschungsarbeiten gewidmet. Zunächst sind es die Möglichkeiten der *Verbesserung der Abscheidung von Staub aus Industriegasen*, die uns interessieren.

Einen besonderen Raum nimmt der Auswurf von *Kleinfeuerungen und des Hausbrandes ein*. Die Feststellung der Größenordnung des Staub- und Rußauswurfes und die Möglichkeiten einer Verminderung durch konstruktive, brennstoffseitige oder feuerungstechnische Maßnahmen sind der Inhalt einer Reihe begonnener Arbeiten.

Auf der Gasseite beschäftigen sich unsere Arbeiten insbesondere mit dem *SO_2-Auswurf* aus Industriefeuerungen und Hausbrand, besonders im Zusammenhang mit der Zunahme von ölgefeuerten Anlagen. Die völlige oder teilweise Beseitigung des Schwefels aus dem Brennstoff oder des SO_2 aus den Abgasen mit wirtschaftlich tragbaren Mitteln wird auch weiterhin eine unserer wichtigsten Aufgaben bleiben, wenn auch die Schwierigkeiten sehr groß sind. Eine andere Spezialaufgabe stellt die Verbesserung der *Auspuffgase von Kraftfahrzeugen* dar. Umfangreiche Arbeiten des Verbandes der Autoindustrie haben das Ziel, den CO-Gehalt, den Benzpyrengehalt und den Gehalt an brennbaren Bestandteilen in den Auspuffgasen herabzusetzen.

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5. DIE RICHTLINIEN

Analog zum Aufbau unseres Arbeitsprogramms sollen auch die " *Richtlinien* ", *die das Ergebnis unserer Arbeit darstellen*, nach den vier Arbeitsschwerpunkten gruppiert werden, also in:

1. Richtlinien für die Meßtechnik.
2. Richtlinien für die zulässigen Immissionswerte (Schädlichkeitsgrenzen).
3. Richtlinien für die Ausbreitungsrechnung.
4. Richtlinien für die Begrenzung des Auswurfes.

Gleich nach der Konstituierung der Kommission wurden die Arbeiten aufgenommen und inzwischen für eine Reihe von Luftverschmutzern *Auswurfbeschränkungen* ausgearbeitet.

In diesen ersten " Richtlinien " ist zwar der Gedanke der Begrenzung des Auswurfes durch die zulässige Immission bereits aufgenommen. Er kommt aber noch nicht allgemein zum Tragen, solange es an genügend gesicherten Berechnungsmöglichkeiten fehlt. Als zulässiger Auswurf wurde daher z.B. für Dampfkessel zunächst ein Wert festgelegt, der mit den heutigen technischen Mitteln unter Beachtung des wirtschaftlich äußerst Tragbaren erreicht werden kann, eine Bedingung, die auch später zusätzlich bestehen bleiben soll, wenn die Immission zum Kriterium der Auswurfbedingungen gemacht werden kann.

Veröffentlicht wurden bisher Richtlinien für den Staubauswurf von *Dampfkesseln* (mit den verschiedenen Feuerungsarten für Stein- und Braunkohle), *für Zementwerke*,

für Erzsinteranlagen und Kokereien (5) und (6). Sie finden bei der Errichtung neuer Anlagen bereits Anwendung. Weitere Richtlinien für die Emissionen der chemischen Industrie, der Metallhütten, der Raffinerien und Hydrierwerke sind in Bearbeitung.

Diese " Richtlinien " enthalten nicht nur die Begrenzungswerte, sondern zeigen auch nach kurzer Darstellung der Technologie des Verfahrens in ausführlichen Vorschlägen Wege auf, wie bereits im Verfahrensgang die Staubemissionen herabgesetzt werden können.

Da die Herausgabe der " *Auswurfrichtlinien* ", die letztlich die Öffentlichkeit am meisten interessieren, nicht an den Abschluß der Arbeiten in den anderen drei Gruppen gebunden waren, konnten hier sorgfältige Studien angestellt und insbesondere die ersten Ergebnisse der Forschungsarbeiten abgewartet werden. In nächster Zeit werden die ersten " *Meßtechnischen Richtlinien* ", und zwar für die Staubniederschlagsmessung und für die SO_2-Immissionsmessung erscheinen.

Verständlicherweise muß bei der Aufstellung *der Richtlinien für die zulässigen Immissionswerte* die größte Vorsicht walten. Nach zweijähriger intensiver Arbeit werden aber nächstens die ersten Richtlinien erscheinen können, die vorläufige Zulässigkeitswerte für die Industrieabgase Schwefeldioxyd, Schwefelwasserstoff und Nitrose Gase enthalten. Auch erste *Richtlinien für die Anwendung der Ausbreitungsrechnung* werden im Laufe des nächsten Jahres erscheinen.

Mit dem Erscheinen der " Richtlinien für die zulässigen Immissionswerte " und der " Richtlinien über die Anwendung der Ausbreitungsrechnung " wird dann auch in den " Auswurfrichtlinien " die Bestimmung über die Begrenzung des Auswurfes durch die zulässige Immission allgemein zur Anwendung kommen.

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THE RE-ENTRAINMENT OF SETTLED DUSTS

R. A. BAGNOLD

(*Received* 8 *December* 1959)

Abstract—The re-entrainment of settled dust deposits depends on a number of variable factors concerning both the internal structure of the wind and the composition and structure of the deposit. Owing to lack of understanding of the nature and magnitude of cohesive forces between fine particles quantitative knowledge is confined largely to the entrainment of particles bigger than 80μ by steady parallel fluid flow.

Under steady conditions the determining property of the wind is the drag it exerts on the boundary surface of the deposit. This drag can be inferred from measurements of the velocity gradient. The threshold wind gradient at which the deposit surface is disturbed decreases with particle size to a minimum of about 100μ. Its increase as the size is further reduced is due in the first instance to the effects of air viscosity. But cohesive effects soon become dominant, and seem capable of increasing the resistance to disturbance indefinitely. Deposits of fine powders can however be readily dispersed by the ballistic impacts of dust particles larger than 100μ; and locally by previous mechanical disturbances which have caused sharp edges of the deposit to protrude into the wind stream.

THE apparently simple question, " at what wind speed will a dust deposit of specified particle size begin to be re-entrained? " cannot be given any answer. A great deal more information is needed both about the wind and about the dust deposit.

The air flow needs to be defined in such a way as to enable an estimate to be made of the maximum fluid impulse likely to be received by the least secure of the exposed dust grains. The mean speed measured elsewhere is no criterion, any more than the wind measured at an aloof meteorological station is a criterion of the strength of the gusts experienced at a given point in a town street.

Information about the dust deposit needs to include not only the grain size but the proportionate distribution of the different sizes present; and also not only how the exposed surface is orientated to the probable direction of attack, but how the shape of the deposit surface may itself create its own gustiness in the local wind. For instance, a deposit settled out of the wind in a wind shadow behind an obstacle may need a considerably stronger wind from the same direction to disturb it than would be needed if the wind, or a single gust, came from a fresh direction. And a deposit in the open would need a stronger wind if its surface were smooth and streamline than if the surface had been broken up by wheels or by boots.

Further, and often most important, we need to know the degree of cohesion between the grains in contact with one another. In the case of fine dust cohesive forces may well be of a different order larger than those of gravity. And the cohesion may arise from a variety of causes, physical, chemical and biological.

Even with all this additional information the answer could not be relied on in all cases, for the question omits to state whether the wind itself consists entirely of air, or of air containing oncoming solid grains whose impact with the dust deposit may play a far more important part than the fluid–dynamic impact of the air.

Few of the above influencing factors are capable of quantitative definition and measurement. So the original question cannot in any case be answered with precision. Some useful ideas about how the various factors enter may however be gained

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from existing knowledge of the simple case in which a steady wind blows unimpeded and undisturbed over an extended streamline surface composed of cohesionless grains of reasonably uniform size. Insight into the general mechanism can also be got from the similar action of a water stream on the loose sediment composing its channel boundary. In both these cases the internal fluctuations due to eddying or gustiness within the fluid are reasonably consistent, for if the boundary is everywhere uniform, the state of internal turbulence is controlled by the uniform texture of the boundary roughness. But even so definite knowledge of the behaviour of dust deposits is confined to those comprised of grains exceeding say 50μ in size, and is unlikely to be extended to smaller sizes until some quantitative understanding of the cohesive forces is obtained.

Two separate processes must be distinguished in the entrainment of settled deposits to form aerosols or hydrosols. A deposit of settled grains in static contact with one another under gravity constitutes a solid body. And the exposed surface of this body has first to be disrupted or "fluidized". Surface grains must be dislodged and set in motion. Frictional forces due to gravity have to be overcome, and a finite threshold of fluid force is necessary to achieve this.

But though the dislodged grain may be set in motion by fluid force components in the direction of the flow, it does not follow that the grain will then be wafted upwards to any extent by upward components of the internal fluid motion. In order that grains may be dispersed upwards by fluid turbulence it is necessary that some at least of the turbulent eddies shall possess random eddy velocities exceeding the fall velocity of the grains through the fluid.

Laboratory experiments in wind tunnels and water flumes show that in the case of deposits of uniform grains the internal eddy velocities within steady undisturbed flow do not attain the required values until the initial threshold flow at which grain movement over the bed begins has been appreciably exceeded. Hence we must, in general, visualize a second threshold flow condition at which dispersion by fluid turbulence begins.

In experimental water flumes, where relatively much greater flow strengths can be attained, a definite suspension threshold in the case of uniform grains can be detected as a sudden discontinuous increase in the measured rate of grain transport (BAGNOLD, 1956). But no positive evidence of grain suspension by wind has been obtained in a wind tunnel when the grains of the deposit laid on the floor are of uniform size. Comparing similar dynamic conditions it seems that the suspension threshold as deduced from hydraulic conditions should require wind speeds exceeding 70 to 80 ft/sec in a small tunnel. And such speeds have not been reached.

Wind tunnel experiments using sands containing but few grains smaller than 50–80μ all show the grains to move as a low cloud whose ceiling does not exceed the height to which the grains would be expected to rise by simple bouncing. The same effect is seen during a desert sand storm in sand country where sand grains less than 50μ are not present in appreciable quantity. The ceiling of the sand cloud rarely reaches shoulder height, and men's heads can be seen unobscured under a blue sky while the rest of their bodies are invisible within the cloud. The whole country being buried under dune sand, erosion of native rock does not take place; and any previously existing dust has long since been carried away in suspension, leaving only the unsuspendable material.

The height of bounce increases rapidly with increase in grain size. Grains 100μ in diameter rise only a few inches, upward velocity components being quickly reduced by the effects of air viscosity. Grains 1000μ in diameter on the other hand may rise several feet in a medium wind.

The quantitative evidence from water flume experiments shows that if, instead of using sands of uniform size, the sands used include a range of smaller sizes down to a few microns the distinct separate threshold of grain suspension can no longer be detected. Suspension occurs simultaneously with the initial disturbance of the sand deposit by the fluid. Both forms of transport take place together. The unsuspended material including all the coarser grades is driven low over the bed, while other material is transported in suspension, the finest grades tending to disperse indefinitely upwards.

This attracts attention to the initial threshold of grain movement over the surface of the deposit in relation to the wind speed on the one hand and to grain size composition on the other.

Under steady conditions of turbulent flow past a boundary of uniform roughness texture the wind speed varies with the distance of measurement from the boundary. And the speed at any distance is determined by the ratio of this distance to the scale of the boundary roughness texture. The universal Prandtl–Karman relation for rough boundaries is

$$u = 5{\cdot}75u_* \log_{10} \frac{30z}{D}$$

where u is the wind speed measured at the distance z from the boundary, D is the boundary texture size, equatable approximately to the dominant grain size present on the surface, and u_* is the so-called " drag velocity " $\sqrt{(\tau/\rho)}$, τ being the fluid shear stress exerted on unit boundary area, and ρ the density of the fluid. Under given conditions therefore the wind speed increases as the log-distance from the boundary.

Much confusion arises from misuse of the classical fluid–dynamic concept of a frictionless fluid. Effects of fluid flow on its boundary are still often discussed in terms of " the " velocity of the fluid in the absence of any statement as to where the velocity is measured. Measured infinitely close to the boundary, the velocity of the strongest wind must be zero.

The effective property of the wind in so far as its flow boundary is concerned is the mean shear stress or " drag " τ it exerts on the boundary. Direct measurements have been made (ZINGG, 1950) of the drag exerted by a wind on a loose grain boundary in relation to the resulting rate of grain movement. But in general this drag has to be inferred from measurements of the wind velocity u. For this purpose it is convenient to introduce the drag τ in terms of a conceptual drag velocity $u_* = \sqrt{(\tau/\rho)}$ which, by relation (1), is proportional to the velocity gradient.

If we take two or three velocity readings at different distances away from the boundary surface, and plot velocity against distance on semi-log paper, as in Fig. 1, the plotted points are found to lie on a straight line. This line cuts the axis of zero velocity at a small distance corresponding to about one-thirtieth of the surface grain-roughness size; which means that on average the speed of any turbulent wind dwindles to nothing somewhere just below the top surface of the grain boundary.

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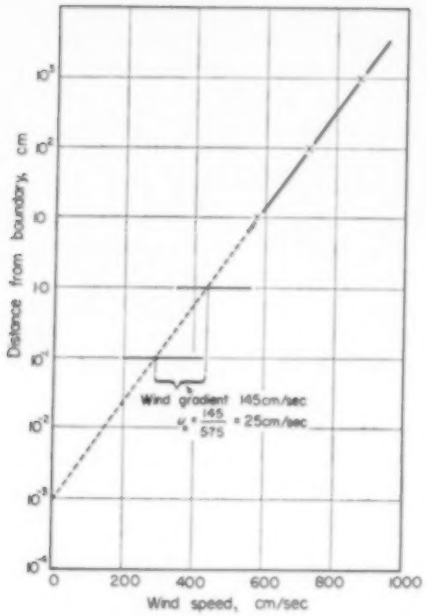

FIG. 1. Relation between wind velocity, distance from boundary and roughness of boundary. The plotted velocities are those of a wind of threshold strength blowing over a surface of sand grains averaging 0·3 mm diameter. The points lie in a straight line which, extended to zero velocity, gives a height of 0·3/30 mm $= 10^{-3}$ cm. The velocity interval between any one cycle of 10 in height of measurement is the velocity gradient, in this case 145 cm/sec. Whence the drag velocity

$$u_* = 145/5\cdot75 = 25 \text{ cm/sec.}$$

The mean wind drag τ on the surface $= \rho u_*^2 = 625 \times 1\cdot22 \times 10^{-3} = 0\cdot76$ dynes/cm^2.

The gradient of the plot is taken as the velocity increase corresponding to any ten-fold increase in the distance of measurement from the grain boundary. And

$$u_* = \frac{\text{velocity gradient}}{5\cdot75} \quad .$$

The drag velocity u_* has the great advantage over the actual measured velocity that it is independent of the distance of velocity measurement.

In terms of u_* the threshold winds which will begin to disturb the surfaces of deposits of uniform and cohesionless grains of various sizes are shown in Fig. 2, taken from Fig. 28 of BAGNOLD (1941). The actual threshold wind velocity at any chosen distance can readily be calculated from relation (1).

It will be seen from Fig. 2 that the threshold of initial disturbance falls to a minimum when the boundary grain size is between 80μ and 100μ. The increase as to grain size becomes smaller than this critical size is not in the first instance due to cohesive effects. It is due to a change brought about by air viscosity in the manner in which the fluid acts on the grain surface.

In the case of considerably larger grains the wind flow immediately over and round the exposed grains is turbulent; and the dislodgement of an individual surface grain

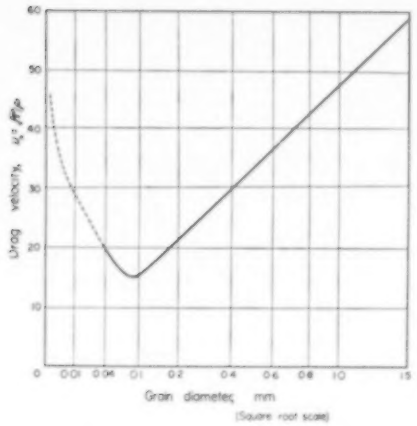

FIG. 2. Threshold drag velocity u_* for quartz-density grains of various sizes. No precise data available for grains smaller than 0·06 mm owing to uncertainty regarding cohesive effects.

is achieved by an individual random buffet the grain receives from a turbulent eddy. But around each exposed grain there exists a thin fluid layer in which the motion of the fluid is viscous. The thickness of this layer is of the order of ν/u_*. Here ν is the kinematic viscosity of the fluid ($\nu = 0{\cdot}14$ in c.g.s. units for air at 20°C). Thus as the surface grains are made smaller, they begin to be entangled and are finally submerged within a continuous viscous boundary layer. When wholly submerged they are protected from the buffetings of the turbulent eddies. The fluid drag is then uniformly distributed over the surface, and individual grains are therefore less easily disturbed.

Another closely associated change takes place when the grain size is reduced below 80 to 100μ. The density of the grains is of the order of 2000 times that of the air. The inertial effects of sand grains, the average of which is say five times as large and therefore 125 times as massive, greatly dominate over the effects of fluid viscosity. Once set in motion by the wind, sand grains, gathering speed, behave like bullets. On descent they impact so violently upon the surface grains as to splash them up into the wind stream. In consequence other grains also behave like bullets, and so on. Thus the chance disturbance of one grain sets off a mechanical chain reaction by which many others are disturbed. Moreover the surface, if previously smooth, becomes pitted by innumerable tiny craters.

But the viscous effects increase relatively at a rapid rate as the grain size is reduced. Below about 80μ fluid resistance to grain motion is relatively so large that grain impacts with the surface fail to disturb other grains. The chain reaction ceases. The change is manifested by a sudden and very pronounced transformation of the sand ripple pattern to a new pattern identical with that seen beneath a flowing water stream. (The quantitative dynamics are discussed in BAGNOLD (1956).)

Hence as we reduce the grain size below about 80μ air viscosity has the dual effect of (*a*) reducing the chances that an individual grain will be disturbed by direct fluid action, and (*b*) preventing the disturbance of one grain by the impact of another.

When all the grains of a deposit have a diameter appreciably less than 50 to 80μ the effects of cohesion due to one cause or another can no longer be ignored. This

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makes quantitative study of the threshold condition very difficult. The gap in our knowledge is suggested by the broken line in Fig. 2.

But the following experiment shows that a reasonably streamline surface of very fine dust is highly resistant to disturbance by wind. When a smooth (uncompressed) deposit of cement powder is spread over the floor of a wind tunnel, the wind can be raised to an experimental limit of 120 ft/sec, measured at 10 cm height, without any continuing disruption of the surface (BAGNOLD, 1941).

Deposits of fine powders can however be easily disrupted where previous mechanical disturbance has caused sharp edges to protrude into the wind stream. If in the foregoing experiment a sharp-edged hole is made in the deposit by dropping a pebble through the surface, the sharp edges will be torn off as lumps by a comparatively feeble wind, the lumps immediately disintegrating into puffs of smoke. But once the corners have become rounded no further disruption takes place.

The effect of a wind on deposits of fine powders can sometimes be observed in open country. Owing to a combination of drought and geology wide areas of plain exist on the Anatolian plateau, near Afyun, where the ground surface consists of an impalpable white powder, in many places wholly devoid of vegetation. Motoring along a road across these plains on days of quite strong wind one is struck by the entire absence of driving dust. Then suddenly a great dust cloud approaches. It originates in a flock of sheep. Their feet make innumerable little sharp-edged holes whose edges the wind is able to tear off. After the flock has passed the air again becomes dust-free.

It seems therefore that dust deposits composed wholly of fine particles are with difficulty re-entrained by a steady wind, provided such deposits if naturally laid down are left undisturbed by wheels, feet, etc., or if disturbed have already been subjected to a wind. One should however make an exception in the case of " fluffy " dusts, whose effective density in relation to their overall size may be extremely small.

If on the other hand the dust deposit contains, as it usually does, an appreciable proportion of coarse grains of ballistic size, i.e. larger than 100–200μ, it will be very easily disturbed by direct wind action. And if at the same time it contains a considerable proportion of very fine grains, an initial disturbance of the easier-moved coarse grades by a wind will result in the fine grades being dispersed upwards in suspension, in spite of a reasonable degree of cohesion. For not only will the fine-grain surface be pitted by the bombardment of coarse grains, but the bombardment is likely to break the cohesive bonds.

When but few of the coarser ballistic grains are present, their dispersive effect is likely to be much greater in the case of a thin deposit resting on hard smooth ground, for example a street or pavement. For the coarse grains will then continue active instead of becoming buried within the fine material.

It is rather doubtful how far the evidence obtained from experiment in which the strength of a steady wind is gradually increased is really applicable to the case of a sudden gust. The gust condition envisaged is that of an intruding lump of air moving at high velocity by its own inertia and creating an advancing front. The dynamics involved in this case may be very different from that in the case of a whole column of air accelerated through a wind tunnel. The Mach number may be far less than unity and the static pressure gradient in the direction of air movement negligible, but the dynamic pressure gradient may be very considerable, as we know from the

sudden impact of a gust upon ourselves. Experiment on these lines would seem important, with a view to establishing the truth or otherwise of one's instinctive notion that a sudden " pouf " is more effective in dispersing dust than a steady blow.

In conclusion I would like to emphasize how little we know about the causes and effects of cohesion between fine particles. Consider for instance this very simple example. Let a sample of clean grains of any chemically inert solid material such as quartz be placed, either carefully dried or else wholly immersed under water, in a test tube. And let the tube then be gradually tilted. Whatever the material tested, grains larger than 100μ will avalanche with movement between individual grains when their free surface exceeds a constant and repeatable angle of tilt between say 30° and 40° depending on the grain shape. But grains of the same material smaller than 60 to 70μ will not avalanche. The free grain surface will stand as a cliff, almost vertically; and collapse will take place by the breaking off of discrete pieces of cliff. No satisfactory explanation of this marked difference in behaviour has so far been suggested.

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Reports on Meetings

52nd Annual Meeting of the Air Pollution Control Association

Report of a Meeting Held at Los Angeles, California from 22–26 June, 1959.

The Air Pollution Control Association met in the Statler-Hilton Hotel in Los Angeles to hear a total of seventy papers presented in sixteen sessions. Dr. LEONARD GREENBURG was installed as president of the organization, replacing Mr. ARNOLD ARCH. The opening session, presided over by Mr. S. SMITH GRISWOLD, included keynote speeches from a diversity of viewpoints. California State Senator RICHARD RICHARDS, representing state governments, discussed the (then pending) state law requiring the Department of Public Health to set standards for auto exhaust emissions and for community atmospheres. Mr. ERNEST HART, representing the Manufacturing Chemists Association, took issue with state regulation of air pollution. It is the view of MCA that regulation should be at the local level, with the state and Federal governments providing technical assistance and advice only.

Dr. DAVID E. PRICE, Assistant Surgeon General, U.S. Public Health Service, in presenting the Federal point of view, discussed the evidence in the United States and abroad for health effects of air pollution. He pointed to the clear evidence of a relation to chronic bronchitis in Great Britain, and to the mounting indications of an association with pulmonary and alimentary cancer. Mr. WARREN L. DORN, Chairman of the Board of Supervisors, Los Angeles County Air Pollution Control District, presented the local viewpoint. He described progress in control in the Los Angeles area, with particular reference to the recent regulations on the sulfur content of liquid fuels and on the olefin content of gasoline. He expressed the view that control of stationary sources of pollution was the responsibility of the local community in which the sources were situated; however, such mobile emitters as autos could not be controlled within a local jurisdiction, and hence must be a concern of the state government. He was critical of the lack of progress in techniques of exhaust control for automobiles. Finally, the viewpoint of the scientist was discussed by Dr. EARL C. BOLTON, of the School of Law, University of Southern California. Dr. BOLTON, representing President TOPPING, who could not be present, discussed the placement of responsibility for research.

In a session on health aspects of air pollution, J. R. GOLDSMITH discussed the present state of epidemiological studies of air pollution in California. To date there appears to be no individual health effect clearly associated with air pollution in that area. H. E. STOCKINGER discussed the toxicologic interactions of mixtures of air pollutants. He discussed four distinct types of interaction—protective tolerance, cross-tolerance, synergism, and antagonism. Examples of each were presented, and speculations were given concerning the mechanisms involved. C. H. HINE and his co-workers reported on experimental studies of eye irritation from air pollution. Attempts to develop objective measures of eye irritation in experimental animals have been unsuccessful to date.

A group of four papers discussed the problems of control of emissions from flue-fed incinerators in Los Angeles, New York City, Chicago, and Detroit. It was generally agreed that the uncontrolled flue-fed incinerator in most general use in the U.S. is undesirable. Suggested remedies ranged from minor modifications of firing practice to complete abolition of the devices. A session on atmospheric monitoring included reports on the air monitoring networks of Los Angeles County, by W. J. HAMMING and co-authors, and in the State of California, by G. J. TAYLOR. Other papers were on a discussion of monitoring for radiocative materials at the Hanford, Washington, Atomic Products Operation, by J. K. SOLDAT, the use of growing plants for air pollution monitoring, by E. F. DARLEY, and on the use of freon-powered samplers for air pollutants in the field, by L. MARCUS and co-workers from Brookhaven National Laboratory.

A discussion of the problem of organic solvents in air pollution was begun with a review by JANET E. DICKINSON of organic emissions into the Los Angeles atmosphere. H. W. FORD and E. A. SCHUCK outlined the photochemical processes by which organic compounds are changed into the noxious complex known in Los Angeles as " smog ". A pilot plant for the study of the control of organic emissions from surface coating operations was described by C. V. KANTER and co-workers from the Los Angeles County Air Pollution Control District. Arguments for the use of activated carbon and

of catalytic combustion in the elimination of organic vapors were discussed respectively by repre sentatives of manufacturers of the two types of equipment.

A session on radiological air pollution included elementary papers on fallout and on its measurement, by A. W. BELLAMY and C. L. BAURMASH, respectively. Radiological monitoring programs in Houston, Texas, and in Los Angeles County, California, were described by G. GOMEZ and W. A. QUEBEDEAUX, and by A. WILEY and P. S. TOW.

The results of a survey of contaminant emissions from fuel combustion, by R. L. CHASS and R. E. GEORGE, opened a session on the combustion of fuels. R. D. REED contributed a discussion of mechanisms of combustion. D. H. BARNHART and E. K. DIEHL discussed a modification of gas-fired boiler furnaces to decrease the generation of nitrogen oxides during combustion. H. C. AUSTIN and W. T. SPROULL explained the applicability of electrostatic precipitators in the cleaning of the effluents of similar installations. D. BIENSTOCK and J. H. FIELD, of the U.S. Bureau of Mines, discussed the chemical, engineering, and economic considerations in the removal of sulfur dioxide from flue gases by means of solid metal oxides.

A group of five papers were presented on the air pollution aspects of municipal zoning. J. M. LEAVITT discussed meteorological considerations in the evaluation of community air quality potential I. A. SINGER described an objective method for site evaluation, based on a mathematical model which, after suitable field experiments (not yet performed), could be applied to the rating of industrial sites by high speed computer methods. The other three papers, by W. D. HOLLAND, *et al.*, E. A. SCHULZE, and D. A. MUNCY, discussed legal aspects of zoning ordinances.

A final specialized session was devoted to the use of simple techniques in solving common air pollution problems. R. SMITH discussed the use of photography in enforcement. C. W. GRUBER, *et al.*, discussed odor determination techniques. B. LINSKY suggested the use of exposed painted panels for identifying certain pollutants. G. C. HASS and R. J. GRAUL described the use being made in the State of California of the " high volume air sampler " which is also widely used in the United States by the U.S. Public Health Service and others.

In addition to the symposia on special topics, there were a number of general sessions. The papers presented at the latter are mentioned here in groups according to topic rather than in chronological order. A number of papers were devoted, as could be expected, to specific control mechanisms or techniques. J. L. MILLS and co-workers from the Los Angeles County Air Pollution Control District discussed the design of after-burners for varnish cookers. R. L. STENBURG, *et al.*, of the U.S. Public Health Service described a pilot plant incinerator of extreme flexibility. The effects of underfire air, excess air, charging rate, secondary air flow, and fuel moisture content were carefully studied with this device. C. R. COMPTON and F. R. BOWERMAN, of the Los Angeles County Sanitation District, discussed alternatives to incineration in a paper on waste disposal without air pollution. K. T. SEMRAU presented a mathematical treatment of dust scrubber efficiency. G. T. NICKLIN presented some engineering considerations of the same problem. Specific control measures for hot-dip galvanizing kettles were presented by a group from the Los Angeles County Air Pollution Control District. Another group from the same laboratory described methods for the control of emissions from asphaltic concrete batching plants. There were a series of three papers presented by manufacturers on a variety of electrostatic precipitators.

Papers concerning atmospheric concentrations of air pollutants included a community survey in the vicinity of a beryllium plant, emission surveys in the Los Angeles and San Francisco areas, and a report by C. E. ZIMMER, E. C. TABOR and A. C. STERN of the U.S. Public Health Service on particulate pollutants in the air of the United States.

Three papers related directly to the problem of automotive exhaust emissions were presented. S. L. RIDGWAY described the present status of the Ramo-Wooldridge direct flame after-burner for automobiles. A. H. ROSE, JR. and C. S. BRANDT described the design of the facility presently under construction, for the study of automotive exhaust and its photolysis products, at the Taft Sanitary Engineering Center of the U.S. Public Health Service. J. C. CHIPMAN and M. T. MASSEY described a proportional sampling system for the collection of integrated auto exhaust samples.

In the field of laboratory techniques, R. GOLDSTEIN and co-workers discussed a combustion method for determination of solvent vapors at low concentrations, developed in the laboratories of the Los Angeles County Air Pollution Control District. J. S. NADER and D. R. ALLEN discussed an ingenious method of evaluating the particulate loadings of samples taken on membrane filter tape by measurement of the absorption of beta rays. By removal of the beta source, the device could also be used for

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determining the radioactivity of the samples. H. F. DROEGE and co-workers reported on some methods used in air sampling from automobiles in the San Francisco Bay Area. J. C. PARK, *et al.*, discussed some innovations in the use and evaluation of the AISI automatic smoke sampler in the course of a Public Health Service survey of air pollution in Nashville, Tennessee. Some techniques for the calibration of recording atmospheric analyzers were reported by C. L. GORDON and co-workers.

The aerosol spectrometer developed by A. GOETZ was the subject of three papers. Goetz's own group at the California Institute of Technology reported on the design, performance and interpretation of aerosol spectra. A detailed study in an independent laboratory was reported by P. K. MUELLER and his co-workers from the California State Department of Public Health.

Two papers were devoted to various aspects of the oxidation of hydrocarbons, as studied in the laboratory. K. C. STEIN, *et al.*, of the United States Bureau of Mines, described the catalytic oxidation of hydrocarbons at concentrations in the range to be expected in automobile exhaust. A large number of metal oxide catalysts were screened and a few selected for further tests. L. A. RIPPERTON of the University of North Carolina presented some preliminary evidence indicating that compounds as inert as aliphatic hydrocarbons can be dehydrogenated in the air, under appropriate conditions, to yield mixtures of much higher unsaturation. There was even some evidence of cyclodehydrogenation to form aromatics.

Two papers concerned themselves with the effect of air pollution on vegetation. H. C. MCKEE and F. W. BIEBERDORF of the Southwest Research Institute in San Antonio, Texas, used vegetation symptoms as a measure of air pollution in Houston, Texas. They also reported on the chemical analysis of leaves in the presence and absence of pollution. Thus vegetation can serve, subject to proper interpretation, as a sort of long-period integrating sampler. H. T. FREEBAIRN reported on research at the University of California at Riverside on the use of Vitamin C sprays for protection of certain plants from damage by Los Angeles " smog ".

Finally, a paper by E. R. HENDRICKSON of the University of Florida summed up the present status of graduate education for air pollution control personnel. Dr. Hendrickson expressed the opinion that there were presently enough universities offering courses in this field. He stressed the similarity of the needs of air pollution control engineering to other areas of environmental hygiene. He concluded that the present universities, by adding a small number of new courses and slightly reorienting a few others, could meet all forseeable needs for training of personnel, providing personnel would seek such training at these sources.

Ample provision was made for informal discussion sessions, sociability, and plant tours.

JAMES P. LODGE, Jr.

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Int. J. Air Poll. Pergamon Press 1960. Vol. 2, pp. 367–371. Printed in Great Britain.

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WE are indebted to the compilers of the sources from which the titles listed in this bibliography are selected. The number of papers published is so large that we considered a selection of the more important papers made by one with great experience in the field of air pollution would be of considerable value, a task kindly undertaken by Mr. T. F. Hurley.

Abstracts of the papers listed can be found in *A.P.C.A. Abstracts* Oct. 1959–March 1960 (denoted by " A " and code number) or *Public Health Engineering Abstracts* Oct. 1959–Feb. 1960 (denoted by " P ").

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A Non-Selective Collector for Sampling Gaseous Air Pollutants. Prepared for Air Pollution Engineering Research, ROBERT A. TAFT, Sanitary Engineering Center, Cincinnati, Ohio, 1959

THIS report on work carried out under contract for the U.S. Department of Health by the authors describes the development of a portable equipment weighing 60 pounds for sampling, on two activated carbon columns, all the air pollutant vapours at concentrations of about 150 ppm in volumes of air up to 100 litres.

Under test, complete retention of methane and less volatile hydrocarbons was effected. Difficulties were experienced with the drying agent (magnesium perchlorate) which was necessary to preserve the absorbing capacity of the carbon but which also adsorbed some of the sample constituents. However, good recovery of many constituents was possible.

Although this is the " final report ", the investigators acknowledge the need for further development. Their work can be recommended to those persons interested in non-selective collection of air pollutants. The method has some advantages over the more cumbersome, but more complete collection by freezing at liquid air temperatures.

A. J. LINDSEY

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